U. S. Department of Energy
Environmental Control
Symposium

Washington, D. C., November 28-30

PROCEEDINGS

Volume 1 of 3. Plenary Session
Fossil Fuels

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Environmental
Control Symposium

November 28-30, 1978
Washington D.C.

Volume 1. Plenary Session and Fossil Fuels

Organized by
Assistant Secretary for Environment
Office of Environmental
Compliance and Overview
Environmental Control Technology Divisio
U.S. Department of Energy

Coordinated by

Argonne National Laboratory
9700 South Cass Avenue

Available from:

These proceedings document the presentations given at the firs
Environmental Control Symposium sponsored by the Department of Energy
Although the symposium was organized under the auspices of the Enviro
mental Control Technology Division, Assistant Secretary for Environme
Symposium presentations highlighted environmental control activities
span the entire Department of Energy.

The plenary session topic, "Energy and Environmental Goals: C
patibility through Environmental Controls," reflects the Department o
Energy's goal and commitment to the support and development of energy
tems that are environmentally acceptable. This commitment is, in par
shown by the extensive support of environmental control activities wi
the total DOE program: about $300 million in FY 1978*, with a simila
amount anticipated for FY 1979.

The objectives of the Environmental Control Symposium were: (
emphasize that, concurrently with the development of energy technologi
DOE is deeply concerned with the corollary measures required to mitiga
potential impacts on the environment from existing and new energy sys
and (b) to provide a forum for the dissemination of information and
achievements of DOE activities in the area of environmental control.
this reason, the Symposium presentations focused on DOE-supported act
related to research, development, and demonstration of processes, pro
and strategies to eliminate or reduce undersirable environmental impa
of energy technologies. Rather than simply identifying potential pro
areas, the presentations were intended to emphasize results of ongoin
efforts. Symposium topics included discussions of (a) simple "add-on
control methods for application to conventional and possibly emerging
systems; (b) in-process modifications to energy production techniques
control environmental impacts; (c) alternative energy systems; (d) en
mental control aspects of energy transmission, transportation, and st
and (e) alternative energy and environmental control strategies.

Owing to the varied topics covered in the Symposium and the to
length of the papers presented, these proceedings have been arranged
three volumes, whose contents correspond to selected areas of interes
The arrangement is as follows:

The Department of Energy feels that this first Symposium and
sequent symposium now being organized will provide a forum for enhar
information exchange between the Department and the public on its pr
toward the goal of ensuring that the Nation's energy demands can be
an environmentally acceptable manner.

(U.S. Department of Energy unless otherwise indicated)

Session No.	Chairman	Co-Chairman
(Plenary)	Dale Myers, Under Secretary, U.S. Department of Energy	
	Fossil Fuels	
2	W. E. Warnke Energy Technology	Myron Gottlieb Environment
7	William Mott Environment	Bernard Baratz Energy Technology
10	William Peters Pittsburgh Energy Technology Center	Fred Witmer Environment
12	Ralph Scott Pittsburgh Energy Technology Center	G. L. Wiesenfeld Environment
15	Stephen Freedman Energy Technology	Jerry Pell Resource Application
	Nuclear Energy	
3	John E. Baublitz Energy Technology	George Sherwood Energy Technology
6	R. W. Ramsey, Jr. Environment	A. F. Kluk Environment
9	Sheldon Meyers Energy Technology	H. F. Soule Energy Technology
	Transportation	
11	Daniel P. Maxfield Conservation and Solar Applications	Martin J. Bernard Argonne National Lab
13	Robert Flugum Energy Technology	George Chang Energy Technology

   Chairman: Dr. Dale Myers
              Under Secretary
              U.S. Department of Energy

   Keynote Speaker: Dr. John F. O'Leary
              Deputy Secretary
              U.S. Department of Energy

   Plenary Speakers: Ruth Clusen
              Assistant Secretary for
              for Environment, DOE

              Eric Willis, Deputy Assistant
              Secretary for Energy Technology, DOE

              Omi Walden
              Assistant Secretary for Conservation
              and Solar Applications, DOE

SESSION 2*

Fossil Fuels -- Precombustion

Fossil Fuels -- Advanced Methods I (Liquids)

1. Environmental Control Aspects of Coal Liquefaction
   Processes, Lorenzi, Lloyd, and W. Peters, U.S.
   Department of Energy, Pittsburgh Energy Technology
   Center.*

2. Screening Coal Gasification and Liquefaction
   Process Streams for Possible Hazardous Compounds,
   Schmidt, C.E., and M.S. Edmunds, U.S. Department
   of Energy, Pittsburgh Energy Technology Center.*

3. Methodology Development for the Determination of
   Polycyclic Aromatic Hydrocarbons (PAH) in Fugitive
   Emissions from Coal Liquefaction Processes, White, C.M.,
   and A.G. Sharkey, Jr., U.S. Department of Energy,
   Pittsburgh Energy Technology Center; and M.L. Lee
   and D.L. Vassilaros, Brigham Young University.*

4. Integrated Compliance and Control Technology
   Research Activities for in situ Fossil Fuel
   Processing Experiments, Farrier, D.S., et al.,
   U.S. Department of Energy, Laramie Energy
   Technology Center. . . . .

5. Assessment of Control Technology for Shale Oil
   Wastewaters, Mercer, B.W., et al., Battelle
   Pacific Northwest Laboratories. . . . .

6. A Strategy for the Abandonment of Modified
   in situ Oil Shale Retorts, Fox, J.P., and
   P. Persoff, Lawrence Berkeley Laboratory;
   and M.M. Moody and C.J. Sisemore, Lawrence
   Livermore Laboratory. . . . .

7. Subsurface Disposal of Oilfield Brines and Petro-
   chemical Wastes, Donaldson, E.C., U.S. Department
   of Energy, Bartlesville Energy Technology
   Center. . . . .

SESSION 12

Fossil Fuel Power Generation -- Advanced Methods (Gasification)

1. Wastewater Treatment for Coal Conversion Plants,
   Klein, J.A., et al., Oak Ridge National
   Laboratory. . . . .

*Paper not submitted for publication in Proceedings.

SESSION 15

Fossil Fuel Power Generation -- Advanced Methods (II)

*Paper not submitted for publication in Proceedings.

PLENARY SESSION
ENERGY AND ENVIRONMENTAL GOALS:
COMPATIBILITY THROUGH ENVIRONMENTAL CONTROLS

Chairman: Dr. Dale Myers
Under Secretary
U. S. Department of Energy

Keynote Speaker: Dr. John F. O'Leary
Deputy Secretary
U. S. Department of Energy

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Assistant Secretary for Environment
U. S. Department of Energy

Eric Willis
Deputy Assistant Secretary for Energy Technology
U. S. Department of Energy

Omi Walden
Assistant Secretary for Conservation and Solar Applications
U. S. Department of Energy

DALE MYERS

My name is Dale Myers. I am the Under Secretary of the Depart of Energy, and I'd like to welcome you all on behalf of the Secretary myself. Jack O'Leary will do his own welcome here very shortly.

I think you will find that this Conference is further evidence DOE's dedication and really sincere devotion to the principle that en technologies must be environmentally safe. From the basic research fe we're determined to be alert to the environmental impacts of our new nologies, so that when these technologies are ready for the marketpla they will have built into them the protection against dangerous pollut or any other of the environmental ills that come with many of these ne technologies. We will then be in the position that we understand the remaining problems that are involved and how they balance against the picture.

Our environmental group is an integral part of our new develop technologies. We have brought them into the actual process of approvi new technologies and new supply initiatives so that, as we move forwar in what we call the definition phase of new programs, environmental i will come right at the beginning, where we will know what problems are ahead of us and can fold them into the development process for new tec That is a key element of the environmental activities of the Departmer Energy in their relationships with all the other elements of the gover that are involved in the environmental aspects. We expect them to re- present the environmental view in the balance that we are looking for new technologies. And I say <u>balance</u>, very strongly underlined, becaus <u>balance</u> is what we're looking for. Our environmental goals cannot be allowed to constrain unduly the benefits we so sorely need from our er systems. That very difficult balancing act is the act that we have te carry out in the environmental issues of the Department of Energy.

We are pleased that so many DOE contractors and representatives of private industry have joined us for this symposium today. We can look forward to advancing our DOE environmental goals significantly be all of us together will be focusing on the energy supply issues so vi to our future well-being as a nation. Now it is my pleasure to call the Deputy Secretary of Energy, John F. O'Leary. He's a dynamic leade and has spent many, many years in various phases of the energy supply business, a man who has a tremendous background and, I think, a tremer role to play in our overall energy development.

JOHN F. O'LEARY

Well, it's a pleasure to be with you this morning. I'm going speak very briefly and then we'll spend whatever time is left over fo questions. I want to just briefly reflect upon the real job of the De ment of Energy. As you look around the resource base of this country we have plenty of resources. We've got an enormous amount of coal. we wanted to, we could get by for the next 100 years without using an

resources of
was well demonstrated by the turn of the century. It's a matter
historical interest to me to recall that in the early days of the
Oil Trust, as they penetrated market after market, the only marke
they could not penetrate was the Scotch Petroleum market which wa
by the precursor to British Petroleum from oil shale; and even to
find that in various parts of the world, we have a small but flou
oil shale industry. So, if we had to, we could use the technolog
early nineteen hundreds or the more advanced technology of the 1
and 1950s developed by the U.S. Bureau of Mines or the even more
technologies developed by one or two of the oil companies and me
our requirements for liquids and for gaseous fuels.

The problem before us is not one of sheer resource constr
The problem that we have before the Department of Energy takes o
primary parameters. The first has to do with economics. One of
sons that we do not have a massive oil shale industry in this co
economic. The other reason that we don't have a massive oil sha
is environmental. All of the work that is going forward now in
ment of Energy to bring on new technologies is bounded by these
of considerations: economics on the one hand and environmental
and considerations on the other hand. Indeed, if they are not w
all of our work explicitly--and I think, from time to time, I've
of those who had not taken explicit account of these two primary
conditions--they will go astray. We have been looking at the de
of these technologies -- oil shale, the coal liquids, coal gas --
considered these two conditions from the very beginning of the d
tion work. We have sought, through the Policy and Evaluation gr
the Department to get a much better handle on general costing te
The Under Secretary is now formalizing that by adding into the c
shop a small group that will have the responsibility for providi
better economics than has been the case in the past. We have a
history of overruns of projects that we deal with. I'll give yo
little anecdotal history of the "why" of this. About four years
was with Mitre Corporation, I was going over with Ed Teller a wi
project that had been developed by one of the aerospace companie
told Ed that the cost of this particular machine was on the orde
per kilowatt, or so it was projected by the sponsors. He looked
came up with a much higher figure. I asked him why there would
enormous range between the sponsor's estimates of cost and the e
that he had come up with. (As I recall, it was a factor of 5 or
Teller's response to that was something along these lines. The
of the new technology knows that the cost isn't zero. He realiz
it's going to cost something. However, he wants to keep as clos
as possible, intuitively, and, consequently, he has an overwhelmi
to underestimate the cost.

We have found in our history here of DOE and its precurso
cost-estimating function has been one that has been performed b

tor of 13. So one of the things then that we're going to have to do is
much better handle very early on in the game on our cost estimating; how
as I say, that process is well along now.

The other point that we're going to have to do is very early on,
as one of the selection criteria, we're going to have to know a great de
more about the hypothecated environmental impacts of these projects than
we do at the moment. One of the things that we're concerned about, for
example, is that we go along, spend a great deal of the taxpayers' money
a technology, and find that we have, in fact, created a monster. The po
bility, for example, of carcinogens in relationship to our synthetic fue
work is very real, very high. We are going to have to evaluate by-produ
of the processes that we're developing, and secondly, we're going to hav
to develop,from early on, a control technology. Just last week, we had
review of one of our major initiatives in that field of synthetic fuel.
In the course of that initiative, it became quite clear that we had not
yet brought the Environment Division into the degree that we should have
in the development of the overall project management criteria. As a res
of that review, Ruth's people will now be brought into that project as
active partners from the very outset   to insure that the environmental
considerations are taken into account as the project develops and become
inherent part of the process.

The Department must, within a reasonably short period of time, st
for a satisfactory resolution of these two constraining elements of our
work, that is to say,the economics and the environmental impacts. If we
do not build in, from the very beginning, means of environmental control
we will not have served the public in the work that we are doing.

Going back to my original point, there are plenty of dirty techno
around. We can meet all of our requirements for energy by simply sacrif
ing air quality, environmental quality generally, and public health and
safety considerations. That is not the name of the game that we're invo
in here. What we are going to try to do, and quite explicitly rather th
implicitly over the next few years, is put in place criteria that will
produce technologies that are economic and that are environmentally acce
able. I regard these challenges as the principal role in R&D for the
Department of Energy. I hope you have a great conference.

DALE MYERS

Thank you, Jack.

I'm surprised you let him off so easy. He's gone now. Now, to g
further into the program. We wanted you to have the opportunity to meet
the Assistant Secretaries of the outlay programs and to hear from them f
a few minutes about their activities. What I'd like to do is to have
the three who are here give you a picture of their activities as they
affect this overall picture of new supply. Please hold your questions u

Thank you, Dale, very much. I, too, welcome the opportu
before you this morning to tell you something about the mainst
energy technology thrusts. Jack O'Leary laid a very good fram
in a sense, for these remarks I'd like to make to you. Our ene
nologies are driven, as he had mentioned, by two things: balanc
economics on the one hand, and getting the new energy technolog
environmentally acceptable fashion on the other hand. Clearly
to be in balance. If you have all volts and no amps, you have
If you have all amps and no volts, you have zero power. So cl
got to have a balance between two. You've also got to be extr
in this balance that you just don't do everything rather like
medicine, where we are finding at the moment that the cost of
is going up astronomically because everybody is practising def
rather than run the risk of getting sued. There is a challeng
to develop technologies which are on the one hand economic and
other hand, do not leave the legacy that we're finding in othe
of environmental cancer. In energy technology, we are advanci
variety of fronts. We span the spectrum of technologies start
which at the moment is everybody's friend, although I've just
from Israel where I've seen solar roof panels for hot water he
top of every house, and I'm sure that they don't make an envir
acceptable picture. Nevertheless, in solar we do have the pro
technology which is perceived to be clean and people can feel
fortable about. But one of our biggest thrusts is in developi
most abundant resource. And that is coal, as Jack O'Leary poi
Today we could just burn coal --we could stuff it in boilers a
burn it, and in that rough manner we could substitute coal for
gas. But as the years have progressed and our air pollution a
become more and more acute, as exemplified by the Clean Air Ac
New Source Performance Standards, we are getting more and more
a nation that we just cannot get hold of coal, stuff it in boi
this neat substitution. So the bulk of our technological thru
to devise methods of using coal in a number of forms so that i
in fact, meet all the New Source Performance Standards and giv
which will be socially acceptable.

Let us review those coal technologies for a moment. I'
come up in the discussions later on.
With coal, you can either clean it up at the front end,
ciation; you can clean it during the process of combustion its
atmospheric fluidized bed; or you can do it at the back end of
with scrubber technologies. You can convert the coal into oth
You can convert it into gas, which has a lot of attraction. Y
doing two things: not only are you converting it into an envi
acceptable product, but you are also converting it into a tran
medium making use of the large capital investment which exists
natural gas pipeline distribution system. So we are concentra
heavily on coal gasification as a hedge for the future when ou

future in an environmentally acceptable manner, taking out the pollutants at the same time, ensuring that our transportation sector and the industr which uses the fuels are properly addressed.

Now let me turn for a moment to one of the most vexing questions haps on the environmental scene today, and I see from the program that th going to be discussed in two further sessions, and that is the nuclear pr We have to almost ask ourselves at this stage, what is the future for thi energy source? Nuclear, as you know, has essentially three problems to satisfy. One is the inherent reactor safety problem. The second is the nonproliferation function and the third, but by no means least, is the radioactive waste disposal problem. We are trying as best we can to insure that all three of these environmental problems are addressed. Th is not a small undertaking. It's, in fact, a very difficult undertaking It needs a lot of interaction with the public. It needs a lot more knowl than we have today about how to store radioactive waste in a manner which will not be a legacy of disaster for future generations. These things we are conscious of and these things are driving in large measure our tech- nological investment strategy. I want to dwell on that point for just a minute. We are not in the business of just spending taxpayers' dollars. a hard-earned dollar, it's your dollar, it's my dollar. What we are attempting to do is to invest that dollar so it has the greatest return on the investment for the U.S. taxpayer-that it exerts the greatest lever possible. Now, that in turn means that we have to have goals. We have to have fairly well-defined goals because you cannot have a strategy unl you have a goal. And a strategy without a goal is a road map to nowhere So we have to map out a scenario of where we want to be tomorrow so that we can build our investment strategies today to meet those goals. That is part of the big dilemma that faces us in energy technology investment namely, "How do we put our dollars into those things that are going to have the maximum payoff?" We come back again to a balance between the economics and the environment.

We are also concerning ourselves, too, with very far-off technolog We are dealing with the fusion technology which promises to have a payof not in this decade or perhaps not in the next decade, but we are contemp ing a long-term technology for which it is by no means obvious that it i going to be environmentally benign. So we have to start right at the ve beginning in every technology we undertake to insure that the environmen factors are taken into account.

I just want to conclude by assuring you that in our consideration of projects, we shall look very, very carefully right from the beginning not just at the cost and the economics, but what that technology is goin to do for the environment. We cannot, and will not, go down roads which lead to a technology that society will not accept.

of water, on top of the five jets of water were five ping pong balls,
and the object of the exercise was with five shots to shoot down as many
ping pong balls as you can. There was a big fellow and a little fellow.
The big fellow took aim and he shot down three ping pong balls, which wa
pretty good. So he got his appropriate prize. The little fellow with
glasses like the bottom of Coke bottles took a wobbly aim, and went "BAN
All five ping pong balls fell down! He asked the little fellow how he d
The little fellow said that it was quite simple, since he just shot the
who pumped the water. The moral of this story is that you have to go af
things that drive the system. And what drives the system today is this
balance of technological innovation, economics and environment, and toda
are concentrating very heavily on the environment. Thank you very much.

DALE MYERS

        I'd like now to introduce Omi Walden, who is the Assistant Secret
for Conservation and Solar Application.   Omi.

OMI WALDEN   \

        Thank you Dale. I welcome this opportunity to speak briefly with
you this morning on the relationship between energy conservation, the us
of solar energy, and other disperse technologies and our national enviro
mental governmental goals.

        Conservation and the greater utilization of renewable systems can
contribute significantly toward meeting our nation's goal of improved
environmental quality. Conservation does this, of course, by reducing
the demand for energy services and doing so without necessarily reducing
the output of the product or function desired. In other words, we can a
we must learn to become more energy efficient in our use of our valuable
energy resources. Although it's almost trite to note that the reduced u
of fuel results in less adverse environmental impacts, there is one area
where efficient use of energy is particularly important. That is in the
efficient use of electricity. In general terms, it takes three units of
primary energy resources such as coal to produce and deliver one unit of
electrical energy. Another way of looking at this is that for each kilo
hour of electricity not used because of more efficient equipment and man
facturing processes, three times as much on a Btu basis of potentially
polluting fuels need not be burned.

        Similar environmental advantages can be cited in the case of indu
trial cogeneration of electricity, for example. These conservation con-
siderations assume an even greater importance and, indeed, urgency, now
that national energy policy embodied in the National Energy Act require
the increased use of coal. However, while conservation and environmenta
goals often are more than compatible, environmental goals added as a qui

all the natural gas to help us bridge the gap between the energy requi
ments of today and a time when more abundant and renewable resources
indeed in widespread use, simply increasing coal usage, with the addi
of emission controls to conventional technology, may result in ineffi
operation and, therefore, be insufficient to maintain acceptable envi
mental quality. This means that, in the future, emission controls plu
reduction in demand will most likely be a necessity.

In addition to demand reduction, accelerated commercialization
systems for greater use of renewable resources is necessary. Some of
such as orientation of design structures for passive solar heating an
heating domestic hot water, are technically feasible, and in many case
economically competitive on a life cycle basis today, if only we can
the ways to encourage their rapid widespread use in today's society.
whole DOE Conservation and Solar Application's program, then, focuses
the commercialization of these applications and technologies which wi
assist us to reduce one energy demand and substitute these renewable
resources where economically feasible for fossil fuels. Within DOE r
Jackson Gouraud, who is our Deputy Under Secretary for Commercializat
initiated a process to identify those technologies which do offer sig
near-term opportunities, both in an energy producing or saving sense,
in a social sense, to meet DOE's objectives. The process involved in
actions with the consumer and environmental groups as well as with in
try, and it resulted in the identification of about twenty technologi
with near-term commercial potential. Nine of these technologies are
responsibility of the Office of Conservation and Solar Applications.
aspect of the work of these commercialization task forces which will
be of most interest to you is the environmental impact assessment per
for each of the twenty technologies, to identify any adverse environm
effects which might impede early commercialization.

One such task force concerned itself with the CS program on re
energy from urban waste. This, to me, is a most interesting conserva
technology in that it in itself is an environmental control. Its imp
tion, however, can result in generation of fly ash, organic compounds
trace noxious materials. It would be affected by the course of futur
control legislation and may require environmental control technology
limit air emissions.

Other technologies that have had environmental reviews include
hot water and passive solar. No one will be surprised, I believe, to
that both received high marks for posing no insurmountable environmen
health or safety barriers to near-term commercialization. In additi
these task force activities, each CS program area, transportation, bu
industry, solar, is working on updating its environmental development
The EDPs have as their purpose to first, incorporate environmental co
tions into the planning process at the earliest practical stage of te
development; second, insure that environmental issues are resolved co
with the development of the technology; and third, assure that enviro

Federal efforts cannot be effective if undertaken unilaterally. Most importantly, we must work and encourage the private sector to undertake the necessary basic research and development on the very front end and to do it consistent with the three areas that I have just touched on.

Additionally, it's most important, for both us at the federal level and you in the private sector, to understand that a partnership is most important with state and local government. It's integral to the development of successful, environmentally sound commercialization of programs. The states have already demonstrated their capability to develop comprehensive energy management and, certainly, environmental programs. And in many cases, they have supported these efforts with state legislation, which in some instances contain standards more stringent than corresponding federal legislation. Federal programs must complement and encourage the state initiatives and, if we are to be successful in preventing state initiatives which are impeding the development and use of necessary technologies, then we as federal officials must recognize that it is exceptionally important that working with state and local officials can best help achieve both our environmental and energy objectives. Thank you.

DALE MYERS

Thank you, Omi.

To get the overall perspective of the environmental elements of the Department of Energy, we have a great opportunity now to hear from a person who has joined the Department reasonably recently, but who has had a very long and dedicated background of public service and strong interaction with the environment. I'd like to introduce Ms. Ruth Clusen, Assistant Secretary for Environment for the Department of Energy.

RUTH CLUSEN

Thank you. This is my first opportunity to say "Welcome" to those of you who are attending this Symposium and to say that I hope these three days will be informative and rewarding. Although this is a total DOE event, of course, it was the responsibility of my office to organize it, so in a way, I'm your hostess. I can't resist pointing out to you that, etymologically speaking, the word symposium means drinking together, so these sessions should also prove stimulating. Without the support of the rest of the Department, the other Assistant Secretaries, and their staffs, we would not have been able to do this, and indeed, their graciousness in serving as Chairmen and developing papers and in working out the necessary details is very much appreciated, and I especially want to thank the Under Secretary, Mr. Meyers, for chairing this Plenary Session, and I later will express my appreciation to the Deputy Secretary, Mr. O'Leary, for keynoting this session.

we also are appreciative of the efforts of the Argonne National Labora[tory] and most of all, I appreciate the work done by my own Division of Envi[ron]mental Control Technology, which has carried the burden for this.

Interest in this topic is not limited to the Department of Ener[gy] alone, and we would especially like to take note of the interest of t[he] Environmental Protection Agency which underlines the cooperation, the interaction, the support of federal agencies in environmental controls energy systems whereever the question is being worked on. Besides EPA there are, of course, any number of other agencies involved, including Department of Interior, the Nuclear Regulatory Commission, the U.S. Ge[ologi]cal Survey, the Coast Guard, and many, many others. I think this all [sums] up that it is necessary that all affected units of the federal establi[sh]ment work together to ensure that the development of energy systems d[oes] not lead to the degradation of our environment. I believe, indeed, th[at] we are working together and that we shall continue to do so for the pr[otection] of the environment. I feel greatly strengthened by the statements wh[ich] have been made this morning by those who have preceded me from the Dep[artment] of Energy who have emphasized that it is balance we are seeking and th[at] they are fully aware of the need to meet environmental needs as we mee[t] energy needs.

The emphasis of this Symposium is not on the total federal cont[ri]bution; rather its purpose is to highlight the Department of Energy's extensive environmental control activities which are carried out in co[n]cert with the development of energy systems and to get out informatio[n] about those activities along with the Department's accomplishments. T[hus] this Symposium is an important part of the Department's and of my offi[ce's] efforts to reach out, to let all the segments of our society know what we are doing, how we are doing it, and what the taxpayers are getting [for] their money. Just as important is our reaching out for information, [ideas] and philosophies to help us better do the job given us by the citizen[s] of this country through their elected representatives. This is one wa[y we] can demonstrate it.

The Plenary Topic this morning, Energy and Environmental Goals [:] Compatibility through Environmental Controls, capsulates the aim of t[he] entire Department of Energy as it goes about its mission of enhancing existing energy sources while developing new and renewable ones. The joining of energy and environmental goals is taking place throughout t[he] Department of Energy, not just in the Office of Environment. Our miss[ion] is to help shape the final policy on each energy source as well as to [aid] in the planning of the research and development and the demonstration of those energy systems. Whenever an energy system is placed in opera[tion] there will be some kind of residue, air emissions, water effluents, o[r] solid waste. Thus, air, soil, water, and people will receive those residues and those wastes to some degree. Obviously, conventional wis[dom] suggests that there is a limit on how much they ought to receive. How much they receive will be established ultimately by rules and regulat[ions] most of which are set by others outside the Department of Energy and [more] important, by perceptions in the minds of the public of what residues ought to be received or absorbed.

mental controls. The broad function of Environment is to provide the De
ment with independent judgments about the environment and its protection
we in Environment must not only look at controls but at research that ca
contribute to the establishment of acceptable environmental standards, a
though in the main, these standards are set by others. So we make envi
mental assessments to look at the products of research. Also, we provid
occupational safety criteria as guidance for those establishments opera
either by DOE or its contractors.

Another environmental function contributes to the formulation of
policies that bridge energy sources and environmental concerns. That me
that the people of Environment and its laboratories and contractors must
consider both energy and the environment; they must have real knowledge
about both.

The primary energy developers within DOE are not in the office of
Environment. Those primary developers, however also have environmental
control activities. Thus not all control activities fall under the Offi
of Environment. In fact, there is big money being spent for that in the
offices of other Assistant Secretaries. The DOE commitment to environme
control, research and development, and demonstration assures that energy
systems will be deployed in an environmentally acceptable fashion. Ther
fore, environmental controls must be developed as an integral part of ea
technology. DOE's understanding and evaluation of environmental control
are important components of responsible policy formulation. Forming tha
policy entails tradeoffs between energy goals and environmental goals.
That really sums up the theme of this Symposium-- balancing energy and
environmental objectives - and a difficult balancing act it is. I think
that one way of explaining it is to think about children on a playground
and how the little kid on the see-saw could increase his fun against the
big kid on the other end. Even though kids don't know the laws of physi
they early discover that they can adjust the situation so that the big k
has less on his side than the little kid does. The word, of course, is
fulcrum, and most kids don't know that. But intuitively, they do know
about balance. Well, it takes a little longer now for scientists and
engineers to decide where to place the fulcrum of environmental controls
balance energy on one side and environment on the other. Yet, that is w
is being done within the Department of Energy. We have been a nation of
doers, scientists and engineers, not to mention the "seat of the pants"
inventors who have collaborated to build and propel the structures and
machines that have made the United States preeminent. And for the most
part, we have had the raw materials right here within our borders. But
along came the environmental movement and the energy crunch, and along w
these came the realization that there was more to consider than just pro
ucts of technology. There were, there still are, hard choices to make a
fueling, heating and cooling these creations of our technology. Dealing
with residues and waste transcends technology. There is strategy in
deciding not to do something, as well as in deciding to do something: t
decide whether to burn coal rather than oil; to decide whether to build
power plants near mines rather than in cities; to decide on a site for a
plant here, not there. So in addition to procedures, processes and syst
environmental controls must also involve strategy. Environmental contro

while still producing energy economically.

DOE involvement in environmental controls covers all of the tech
nologies. You've already heard a little bit about that this morning--
fossil, solar, geothermal, nuclear, conservation. The cost is huge.
For the fiscal year ending last September, the spending totaled some
million dollars. Of total DOE outlays on environmental controls, roug
10% was spent by the Office of Environment. About 60% was in the area
of nuclear energy. About 2/3 of that was for waste management. The
rest was in the area of the nuclear fuel cycle and decommissioning and
decontamination.

As for the other big slice, fossil at 25%, coal accounted for mo
than 90% of fossil, with petroleum and natural gas making up the rema
Conservation, geothermal, basic science, and magnetic fusion shared th
rest. We in the Environmental Office must assess environmental
control options and DOE activities to ensure proper emphasis for contr
in DOE's energy research and development. That's so nothing will fal
between the cracks. Let's take nuclear, for example. In the last qua
century, there has been tremendous progress in harnessing the atom, as
the popular phrase goes.With our   more complete understanding of envi
mental control needs, we now see that the question of what to do with
nuclear wastes should have received more emphasis than it did. An imp
function of my Office is to try to look ahead so that in the future we
have to look back to the current period and wonder what might have be
as we are now doing in the case of nuclear waste management.

We in Environment must assess environmental control needs and ev
the tradeoffs or balance among available options. In making recommend
we must consider such items as these: by-product formation, where and
to dispose of flue gas desulfurization sludge, waste water sludge, oil
shale waste, brine. Where and how ties in directly with the site. We
must consider site specificity, the availability and costs of local re
Is there land for disposal? Is there water for cleanup use? What abc
the quality of the water and its availability? We must consider fuel
characteristics: for instance, high grade coal vs low grade coal. We
must consider energy penalties. How much energy is needed to put some
controls into action. In other words, how much nonproduct oriented en
is used? We must consider system reliability. How long can the contr
operate efficiently? What are the effects of the controls on the tota
energy system's reliability? And we must consider system cost. The c
of the controls must be folded into the cost of the end product, wheth
it be electricity, synthetic gas, coal liquids, or geothermal steam.
Cost, ultimately is the bottom line in deciding on controls.

To evaluate controls then, we must look at the entire system at
same time, not at just one pollutant at a time. And we must consider
effect of the cost of the total control system on the energy cost to t
consumer at the end of the line.

tion must be integral to the energy by controls really are not like automobile accessories bought at the corner auto supply shop. They are best put in at the factory. Our activities include the development of a credible data base to permit substantive independent judgments for DOE policy decisions on environmental control capabilities and requirements. A data base cannot be static. It needs constant updating to reflect changes in cost, experiences, standards, national energy needs and uses.

Our activities include examining proposed standards and anticipating new ones, which implies some ability to look ahead ten or twenty years to try to be constantly on the frontiers of knowledge.

We especially need to pay attention to the implications of environmental legislation which we know will affect future standards, such as the Resource Conservation and Recovery Act and the Toxic Substances Control Act. Specific regulations under those laws presently are being established and we will have to take them into account.

In order to address early as well as long-range requirements of energy technology, Environment employs the systems approach to developing data. Take, for instance, the case of reducing noxious emissions from coal-burning power plants. That goal can be achieved by cleaning the coal before it is burned; by changing the way the coal was burned, such as with fluidized bed combustion; or through add-ons such as cleaning the flue gases; or there can be some combination of these. Going even beyond that, the systems approach focuses on the entire fuel cycle, from the time the coal, in this case, is mined through the management of waste heat. That, in turn, entails considering plant and animal life cycles, how to keep cooling waters from becoming too warm for nearby aquatic life, how to best decommission mines and power plants, how to reclaim strip mine land.

Looking ahead, therefore, requires finding methods for advancing the development of mitigating measures within the Department of Energy and the encouragement for finding less expensive, more reliable, and more efficient environmental controls.

Finally, we in Environment must develop evaluations that help set priorities for research, development and demonstration and to do that with available money, for there will never be enough.

In performance of our assessment and overview duties, my office must be committed to independence, we must be unbiased, we must look at all technologies and, as far as possible, make credible judgments about them. Those judgments must be based on all types of control options - - engineering, environmental, economic. The expertise and information needed for making judgments are acquired through funding studies elsewhere and by research done within the Department of Energy. We must minimize duplication, especially in this time of restricted governmental spending. So close cooperation is sought with the offices of other Assistant Secretaries, other governmental agencies and with nongovernmental groups. These inter-

I'd like to mention a couple of the major environmental documen[t]
that formalize our position on environmental issues and needs within [the]
Department of Energy. <u>Environmental Development Plans or EDPs</u>: an ED[P]
identifies environmental issues and research needs so as to guide the[ir]
research and assessment program's planning and scheduling. The objec[tive]
of an EDP is to identify and link key events; technology R&D; and enviro[nmental]
health and safety research programs. Another document is the Invento[ry]
of Federal Energy-Related Environmental and Safety Research. This li[sts]
all federally funded energy-related environment and safety research p[rojects.]
The current edition covers fiscal 1977. Twelve federal agencies prov[ide]
information for the inventory, which gives the data necessary to cond[uct]
overviews of the federal effort in such research. It is updated each [year.]

A third document developed by my Office and especially germane [to]
this Symposium is an annual survey of environmental control activitie[s]
supported by the Department of Energy. The latest edition covering fi[scal]
year 1978 activities is to be published in the next few weeks. I'm
sorry that we do not have it for you at this Symposium.

My office is committed to making energy and environmental goals
compatible. We are partners with the energy technologies and the oth[er]
Assistant Secretaries. We are not in contention with them. This cou[ntry]
must continue to have increasing amounts of energy if our way of life
is to remain the same and, indeed, improve. Still, we must realize, [that]
regardless of the sources of the energy, there will be residues, wast[es,]
pollutants, call them what you wish, even from the benign new energy
sources. You can tell that by looking at your program. In seeking t[o]
control these wastes, we must be vigilant to protect human health and
safety, plant and animal life, the air we breathe, the ground we walk[.]
It's not an easy job. Yet all of us at the Department of Energy are [trying.]
We hope this Symposium on environmental control will demonstrate that[,]
and that you will join us in the effort to achieve these goals. Than[k you.]

DALE MYERS

Thank you Ruth, for the thoughtful review of this theme that we[']
dealing with here today. I would like to open up the Symposium now f[or]
questions. There is a microphone back here. To properly convey the q[uestion]
to the group, you'll have to use the microphone. I would like to sta[rt]
that process now, if there are any questions. We are going to be fin[ish-]
ing the Plenary Session shortly and we'll lose these Assistant Secret[aries]
and their representatives, so now is the time. Any questions concern[ing]
the areas that we talked about? Yes.

QUESTION: (Paraphrased). The question is the radioactive emissions [from]
coal burning. Ruth, do you want to answer that question? (Referred [to]
William Mott, Director, Division of Environmental Control Technology.[)]
ANSWER: Bill says studies of that nature are going on within the env[iron-]
mental programs. You two guys can get together on that. Anything el[se?]

safety and I was wondering, since a number of [...] that reactor safety is not a big problem, I wonder if you could justify what more DOE could do to solve this.

DALE MYERS

I'll paraphase the question. The question concerns safety in the nuclear facilities. Predecessors of DOE and DOE reports have continued to maintain that the safety problem is extremely low or that nuclear power plants are safe; why do you list it as one of the three major elements of problem with the nuclear power plants. Eric, would you want to come up to the microphone and answer that?

ERIC WILLIS

ANSWER: I listed it because it is not something you can dismiss. There is no such thing as an average nuclear accident, therefore, you have to have constant vigilance that you have not left out of the equation some parameter which will lead to a disastrous situation. Now, we have had no adverse record of note in the nuclear power industry. I think they have a lot to be proud of in their safety record. But the safety aspect, however good our record is, is one of its perception amongst the general public. We have to satisfy the public at large, with nuclear power being under the pressure that it is, that we are taking all prudent precautions, not only to operate safely, but to perform R&D to make sure that we have not left some critical loophole uncovered. That's the reason that I focused on the safety issue, and that is the reason we continue to give it continued vigilance.

DALE MYERS

Thanks Eric.

QUESTION: I think this is more in the way of a comment on which I seek other comments from the panel. First of all, I am, indeed, pleased to see the emphasis on balance in the approach to solving the environmental problem. That is most refreshing. I think that, in this country, we find ourselves in the same position as the 42-year old man who weighs some 300 lb., goes to the doctor and he is told that he must reduce, and he recalls that when he left college and played football he weighed 200 lbs; now he says, well, therefore, I can get back to that weight, but he embarks on this by setting out on a program to lose his 100 lbs in 10 weeks. It took him 20 years to pick it up. And I think that that is the sort of thing that we have to recognize; it took us some time (indeed, it's too bad we didn't recognize it earlier) to pick up all this environmental weight, so to speak, and I believe it's going to take us some time and some balance. Now, in that connection, I see a modest proposal, if you will, and I'll structure it about something like the Clean Air Act. We have continuous requirements in the actual Act over a period of two years or three years. The requirements change and tighten up and just about the time the development results in a good system that is starting to perform, we have difficulties of increased tightening of the requirements.

but capital formation is required and capital commitment is required.
The proposal is the following, and I think that it requires legislation.
Over a period of, let us say, five years or ten years, whatever appropri
you set the regulations and they remain level. During that period of ti
whatever commitment is made to new systems, one can use those standards,
and then, they indeed, have a useful life, perhaps 30 years. Over this
30-year period, those systems that were introduced during that interval
could continue to operate under those standards. Indeed, if we learn
new things, as I see we must, in the next interval of time, the environ-
mental standards could be tightened up. But in this manner, one would
know that if he made a commitment to a certain fluidized bed system, for
ample, or to a coal liquefaction system, that if he got it operating in
that 10-year interval, let us say, he knew that he could continue to
operate it, so his billions of dollars of investment could be properly
or prudently committed.

DALE MYERS

ANSWER: It's clear that the uncertainty in the standards has been an
extremely difficult thing for the industry, and a concept, such as the on
that you are mentioning, has been discussed pretty broadly. We have not
been able to establish that as a pattern; it is one of the things that
certainly the oil shale industry, for example, is looking for. We don't
have standards yet that have been directly applied to the oil shale indu
In a meeting that I had with several of the leaders of the development o
oil shale technology, those leaders were saying, "please, please, have t
government establish one set of environmental requirements. We don't ca
how tough it is, but just one that we can depend on for the duration of
the first plant life." And they literally say, "Make it tough, make it
so that it will last, so that we can do our financial analysis and our r
analysis based on that set of environmental standards." We still have n
established that set of standards for the oil shale industry. And so
the industry has a great uncertainty about the cost of the plan.

QUESTION: I'd like to direct a question to Ms. Clausen, please. A word
haven't heard today is "ecology," which is, of course, the study of
environment. What I'd like to know is how supportive is the Department
of Energy going to be to basic ecology? In other words, the study of th
environment which is not directly related to energy technology, at least
not in an obvious way, but that is essential to an environmental under-
standing. How supportive will the Department be of such studies?

ANSWER: (Ruth Clusen) As I have been meeting with labs and lab directo
particularly, this is a question which has come up with considerable fre
as it relates to our support for basic research programs against what we
call the fast turnaround for those problems that we need a quick answer
on. My feeling about this has always been that we must have a mix becau
it is, in a sense, the basic research that underlies, and sometimes quit
by chance, provides the answer to, questions farther down the line. I
think it's impossible to quantify what percentage, what dollar figure,
should be put in basic and then applied research, which is really what
we are talking about. But it is my feeling, and I believe it is of the

Thank you.

DALE MYERS

Yes, I think you'll be seeing a pattern of additional work by the
Department in basic research, not only in the ecology area, but in the
elements of our various supplies. We feel in the past we have done too
much in the way of development of specific technologies and supplies and
not enough basic research, not enough basic and applied research, leadin
to new ways either to develop new technologies or to protect the environ-
ment that results.

QUESTION: I'm Jerry Nelson from Chicago Operations DOE. I've been aske
to identify myself so now I have to rethink my question a little better,
maybe. I would like to direct this to Ruth Clusen, and having heard the
previous question from Witt Gibbens, I maybe think it has partly been
answered.

My question is in reference to the balance of economics vs the
technology development. I've noticed increasing pressures in my work to
reduce baseline environmental requirements. Now, we have NEPA, which
addresses the environmental impacts, but there are also the federal revi
and regulations, the Clean Air Act, etc. and TOSCA and RCRA to come down
So it is very clear that, where there are environmental regulations, we
have to meet these requirements, do twelve-month continuous monitoring,
etc. for the Clean Air Act. But I've noticed increasing pressures on th
baseline environmental requirements. to develop baseline ecological-type
data on a particular site. And the question always comes up, what is
needed; do we need it? How do you justify the need to do these four
seasons studies, etc? And, of course, this is good. We need to be able
to justify it. But I notice increasing pressure. And my question then
relates also to an executive order, I believe it's 12088, the Carter
Executive Order, which revokes Nixon's Order 1172 of December 1973, has
no exemplary requirement for federal institutions to be an example, to
lead in the areas where no laws cover environmental needs. And there is
no requirement for DOE as an agency to stand out and be a leader in the
environmental areas where regulations do not control emissions where we
have no regulated emissions associated with a new developing technologie
and new source performance standards, etc. have not been identified. No
my question is, what is DOE policy in this area and how might it be or
is it planned to be implemented?

ANSWER: (Ruth Clusen) Actually, I think you've asked us several questi
but I'm going to try to answer the one you really asked. You refer to
the President's Executive Order and comment that there are no exemptions
given for the Department of Energy, for instance, in its own sites. Wit
that, I think we would all agree. Let me give you an example of our try-
ing to look ahead where there are no standards set yet. A problem area
that we are working on right now has to do with the emissions of diesels
Some of our first findings, and I know that some of you have contributed
to this, are showing that there may very well be some carcinogens in die

know that EPA is beginning to think about this and, undoubtedly, it will
follow. We are trying to be ahead by doing the baseline environmental
research, the health effects research also, as well as trying to look at
what could be some mitigating environmental control mechanisms. Both of
these things are going on in the Department simultaneously. This is by
way of showing you that we try to foresee what we are going to have to
react to when the time comes. But broader than that, I would like to be
sure to convey to you the idea that we aren't just setting out to meet
the regulations and nothing more. The basic law that governs what we in
the Office of Environment and, indeed, throughout the Government, must
attend to is the intent and the spirit of the National Environmental Poli-
Act. We're now in a lot of areas where there are no standards carefully
laid out in advance, and we are trying to second guess. We, in some ways
deal with the same uncertainties that the gentleman who spoke with such
feeling about the capital investment of the commercialized end of the
deal. We, too, deal with uncertainties and we will, I think, in no way
be trying to lower the base line or trying to seek the lowest possible
level of these things. Indeed, in some cases, we are looking at what cou
be the greatest possible threats or what could be the most stringent regu-
tions which we would have to meet.

QUESTION: I'm Tom Bechtel from Envirotech. At the risk of wearing
Ms. Clusen out, I'd like her to expand a little bit on the relationship
between DOE and EPA because it's obvious you are playing on one another's
turf in two areas. One--future regulation and its impact on energy tech-
nology development; and two--environmental control technology development
How do you interact in the planning area in those two areas?

ANSWER: (Ruth Clusen) As for the relationship between EPA and the Depar
ment, on my part its friendly, and rather close. I think it serves us
all well when we have this kind of relationship with the agency that has
to set most of the standards and regulations, and I have spent considerab
time in trying to develop this. The more we know what's in their minds
about the direction they are going in some of these things, I think the
better we can do our job at the Department of Energy. We also try to
encourage them to do work in environmental control technology. This is a
tremendously expensive operation. It seems to me, at least, that they
should, in a sense, do what we are doing when you are setting regulations
and looking at, or responding to regulations and looking at what they
demand, you should also be trying to develop the technology which will
help you meet those standards. We are engaged in some mutual ventures,
in fact, in research, and we try not to duplicate what is done. This is
of the factors I think we must all avoid. We often meet together to dis-
cuss this kind of thing, and I think it can be a mutually supportive
arrangement when we approach it that way.

DALE MYERS

Let me give you an example of the kind of thing that we work with
the EPA on. EPA has had the development of new scrubber technology for
coal plants; and we, on the other hand, have been working across the
whole spectrum. As Eric Willis said we work all the way from the cleanin

try to strike a balance between some cleaning at the front end and the
costs involved in the final scrubbing. All of that activity is balanc
in the Department of Energy. We have the opportunity in our technolog
developments to broaden that spectrum further than the EPA activities
processes. But, on the other hand, the EPA has had some very basic de
ment work in scrubbers; and we have a very close liaison with them so
that we do not duplicate this technology. I think you will see, by th
way, cases where it appears that there is a major conflict between EPA
and us. There has been, for example, strong interchange of basic data
on such things as the coal emission standards, because of our knowledg
and understanding of the reliability of the scrubber technologies, and
the emissions of various levels of sulfur in the coals themselves. So
there is a play, back and forth, and there is a balance with DOE tendi
to lean a little more towards the energy side, and EPA leaning a littl
more towards the environmental side.

QUESTION: I'm Ken Wilzbach of Argonne National Lab and I'd like to als
direct a question to Ms. Clusen. It disturbs me as an individual to se
environmental legislation enacted to achieve political objectives as
opposed to environmental ones, and some of the regulations being promul
are designed to force the development of technology rather than primari
designed for protection of the environment. Is this one of the policy
issures that DOE is addressing?

ANSWER: Could you give us an example of what you had in mind?

QUESTION: Such as those sections of the Clean Air Act Amendments desig
to maximize the use of local coals.

ANSWER: (by Ruth Clusen) I'm not going to say I'm glad you asked that
question. I'm going to say that's a hard one to answer because you are
referring more to the implementation of legislation in the guideline se
ting than to the passage of legislation, it seems to me. Your quarrel
may very well be with the Congress, and not with the Department of Ener
or the Environmental Protection Agency, I think, in that case.

QUESTION: I'm Lennie Fedder with UOP, Inc.,and I also have a question
Ms. Clusen. You're just popular. I was wondering if you could give a
little more information on the breakdown, mainly with respect to scrubb
technology, between EPA and DOE. We had heard that there was, back in
the spring, $14 million worth of funds that were going to be transferre
and technology was going to be transferred between EPA and DOE. I've
also heard that this was going to end up in ET. Exactly what is the
status on that whole area, please.

ANSWER: (Dale Myers) Let me speak to that one. There was an agreemen
with the Office of Management and Budget that there would be control
technology funds transferred from EPA to DOE, and that there would be
some health physics, basic health science, transferred to EPA. The idea
was that there was a nucleus of capability in EPA that OMB felt should
expanded, and there was a need in DOE to expand the control technology,

in its wisdom did not agree with us.

We've had some difficulty since that time sorting the problem ou
think that eventually we will, because what we are talking about does,
think, make sense. Probably one of the impacts that you got was a maj
mechanical flap in the system at the end of the fiscal year, because w
ended up without an appropriations bill for a few days. That really m
a problem, just paying salaries of some of the important physicists an
science people who were involved in that program. We did get that st
ened out. We still have some work to do in getting that whole issue
balanced out. Anything you want to add to that, Ruth? (no response).
It's back in the court of OMB right now; It got lobbed there. Any oth
questions?

Let me cover a subject and some material here. It deals basical
with the National Energy Act. The NEA was finally passed after eighte
months of terrific infighting within the Congress, dealing with subjec
that I think probably you are all aware of, subjects that had been sor
of sacred, hallowed ground within Congress for many, many years. Such
things as regulation of gas had been in the Congress and on the books
decades, and to change that became regionally important. Because of t
there has been a tremendous amount of debate in the Congress. I think
that, to the rest of the world, it looked as though the United States
couldn't make its mind up on energy policy.

The fact is that we have come out with an energy policy which ha
really done several things. It projects that we will save about two-
thirds of the barrels of imported oil that we had projected when the
administration submitted its plan to the Congress. In almost all elem
of the bill, we got certain parts finished. We didn't get all of any
part. In one area, we bombed out completely, that on the well-head ta
on oil. That means that we do not have the kind or price increase on
crude oil that will have an impact on the use of oil in this country.

There are other things happening that are increasing the price c
We are going to continue to work to get oil to something closer to worl
price, so that the use of crude in the normal financial analysis of a
business will not be as attractive as it is today. What did happen was
that we did get the intrastate and interstate gas prices balanced so th
some caps came off of some wells here and there around the country, and
there is right now what the American Gas Association calls a bubble of
There is more gas available right now and will be in the next two or th
years than we had anticipated in the balanced program that we had subm
to Congress. So that's good from an environmental standpoint; gas is
environmentally very acceptable. In many places now, we are actually
to get utilities and others who have the dual capacity of burning oil a
to burn gas for a while, and then to get over to coal. Conversion of p
from oil to coal is not as strong as the administration wanted it to be
it will have a major impact. So there is going to be a lot more coal b
and there is going to be a need for our very strong emphasis on environ
controls concerning the use of coal.

for the year 2000 by a factor of 4. That means that electrical energy generated by nuclear power is not going to happen, by a factor of three or four, compared to what had been originally euphorically projected, back in 1970 and 1972. That means a lot of things happen. We are going to need other sources of energy than nuclear. We are going to need them probably more than we had originally projected. In order to try to hold down imports of oil, we are going to have to press much harder on the alternatives and the alternatives are gas and coal and the renewables. In the renewables, therefore, you are going to see much more emphasis from the Department of Energy because they are, in general, as far as we can tell, environmentally more acceptable.

Their problem is cost. Right now, solar hot water is good in many parts of the country in places where it is competing with electric hot water heaters. It is marginally good in areas of space heating in certain parts of the country but for air conditioning, it's just not there yet.

So we have a lot of research going on trying to drive down the cost of these alternate renewable activities. The renewables go beyond these basic sort of "heat" processes of solar energy and move on into the important renewables, such as hydroelectric power and biomass in the form of wood, which is here today and really putting out a sizable amount of our energy. But in the future, we've got to do more with wood, more than with other biomass, more than with what we call low head hydro.

In the areas where dams exist, 50-60 ft head for the water that runs through a turbine is not nearly as efficient as the big hydro dams that we've had in the past, but it is getting competitive, now that the price of gas and other elements go up.

We have a lot of pressure now in the direction of more of these renewable resources. In spite of that, we're going to have a tremendous amount of emphasis on the clean burning of coal, so I think that this is kind of the balance that we're looking for.

There is another fundamental issue about which we in the Department of Energy feel very strongly, but we do not enjoy the support of all the analysts in the country or the world. That is the following: . . . the price of oil is going to vary, not too much, in the next few years. Actually the price of oil has gone down in real dollars in this country since the embargo. It started to go up and then actually in real dollars it has gone down, with the terrific inflation we've had. There is probably going to be a rise in the price of oil in the next year, but it looks like it's going to be very limited. Right now there are a lot of major countries around the world competing in selling oil, and there is not a shortage of oil, so they can compete with each other. They kind of balance out and are still able to yield big incomes for the Middle East countries, Indonesia, Mexico, and so on. This is very important to their economy.

been almost without energy, and the developing countries are beginning really to swing into the use of energy strongly, and they're using oil. So we're going to end up in about the 1985-90 time period with a demand that exceeds the supply.

Pick a number, some say as early as 1983, some say as late as 199[5] to me that's the same time period because with the kinds of things we try bring on as new major supplies, it takes 30 years to make what I call an operational capacity out of those systems. Nuclear energy is just now making a major dent in our energy supply and it's been developing for th[irty] years; the coal plants took that long when they came on-line, and all the new systems we see coming in take a very long time to get on line. So whether it's '85 or '95 really doesn't make any difference. We're going [to] get into this shortage situation again, it's going to drive us much harde[r] in conservation, it's going to drive us much harder in the renewables. [It's] going to drive us much harder in coal. Eighty per cent of our reserve energy in this country is coal and we're generating 18% of our energy wit[h] it. There's an area we're just going to have to pay much more attention [to] as time goes on.

I think that gives you a feeling of where our pressure is. When w[e] go to work on coal gasification to the point of making a major demonstra[tion] plant, when we go to work on liquefaction of coal to give us liquids out there in 1990 and 2000, it's because we know there is going to be a time when we must use a much broader spectrum of other energy technologies than those that have been our standard for the country for the last 60 years.

QUESTION: I'd like to help out. My name is Toby Anthony, Research Cont[rol] I'd like to help out with that question before this one that was just asked about the politics...every national program is political in charac[ter] I think what's missing in this program that we have now, which is Enviro[n]mental Control, is that we've never quantified it...we don't have an agr[ee]ment, a consensus as to how much pollution control will be required to protect our health and safety. If we look back in history almost every national program we've had, except for one that I can think of, had a consensus over what those quantification goals should be: whether it was World War II, landing a man on the moon, or even achieving a high standa[rd] of living. We usually knew in quantitative terms what we were going for[.] I think the problem we have here in the environmental movement is we hav[e] not spent the money and we have not done the work necessary to quantify those goals. We spent billions on control technology and those people in the pollution sources are not sure when this objective is going to be met, when the billions of dollars are going to pay off in terms of how much money they have to spend. It has created a lot of problems for us in the pollution control industry, it's created a lot of problems for people in the industrial section, and unless we do something about that part of it, I think we're always going to have these confrontations over moving targets. I'm not sure the Department of Energy should take the l[ead]

ANSWER: (By Dale Meyers)   I think that is a noble objective but an extr
difficult one.   I was involved with the lunar program; that was such a
nice neat simple objective--to put a man on the moon and return him saf
It really was a galvanizer of people into a particular objective.   If w
could do the same thing in the environmental area and produce a clean
set of objectives the situation certainly would be much easier.   In the
Department of Energy, we are trying to reach for better basic data from
which policies of that nature can be developed, but it is not easy.   The
is such a tremendous spectrum of technologies associated with the enviro
ment that to be able to understand them, as far as health effects are co
cerned, to quantify them in terms of (should I be crass and say) lives
per year due to the energy--it is a very difficult area to define and
quantify for the purposes of development objectives and levels of activ
We are working towards understanding the problem better; I do not think
we are going to get that answer quickly.

Well I think we're ready for a coffee break.   I see there is coffe
in the back of the auditorium.   I thank you all for your attention.   I
think you're in for a very broad-based symposium here, that is going to
be very helpful to you and to us in understanding our environmental
objectives.   Thank you.

SESSION 2
FOSSIL FUELS — PRECOMBUSTION

Chairman: W. E. Warnke

Co-Chairman: Myron Gottlieb

COAL PREPARATION - AN EFFECTIVE MEANS OF
CONTROLLING COAL WASTES

Wilbert E. Warnke

U.S. Department of Energy
Energy Technology

Sulfur dioxide emissions from stack gases can be simply but effec-
tively controlled by pre-combustion cleanup of coal. Many of the trace
elements commonly associated with coal can also be controlled through pre-
combustion cleanup. In order to reduce sulfur to acceptable levels, com-
plex physical and chemical processes are required in contrast to simple
process used to remove the coarse ash minerals. When the ash minerals and
pyrite are almost totally removed by the newer processes involving fine
grinding and multi-phase separation procedures, elements such as arsenic
lead, zinc, cadmium and others are also removed. Waste products containing
the sulfur and trace elements can be safely stored as land fill. The pre-
sentation summarizes projects and programs presently underway to control
pollution from using coal. It includes a preview of emerging technology.

EFFECT OF COAL CLEANING ON FUGITIVE ELEMENTS.
A PRELIMINARY PROGRESS REPORT

Charles T. Ford

Bituminous Coal Research, Inc.

The coal industry, through its research affiliate Bituminous Coal
Research, Inc., has established a program for obtaining valid information
concerning potential trace element problems as they relate to coal. One
means of controlling trace element emissions is to remove these trace co
stituents prior to combustion during the coal cleaning process. In the
recent BCR study funded by the Department of Energy, twenty run-of-mine
will be subjected to conventional cleaning processes as well as to more
tensive non-conventional processes to evaluate the effect of such cleani
fugitive elements--those elements which might be released to the surroun
and cause environmental problems. Based on the initial results in clean
the first few coals, coal cleaning represents a method for controlling p
tially harmful constituents of coal such as arsenic, cadmium, lead, merc

E.M. Wewerka, J.P. Bertino, P. Wagner, L.E. Wangen, J.M. Williams, ...

Los Alamos Scientific Laboratory

The aqueous drainage from coal piles and coal refuse dumps freq
is contaminated with acids and a variety of trace elements and inorgan
stituents. The Los Alamos Scientific Laboratory is conducting researc
jointly supported by DOE/ECT and EPA, to assess the nature and magnitu
trace elements in the drainage from coals and coal preparation wastes,
identify the necessary environmental control technology for this form
environmental pollution. The current emphasis of this program is on t
oratory assessment of environmental control options for the drainages
high sulfur coals and coal wastes. This presentation will review the
plishments of this research program to date, and discuss the various d
control options available to the coal industry.

IMPLICATIONS OF ANALYSIS OF HIGH GRADIENT MAGNETIC SEPARATION
TO COAL RELATED APPLICATIONS

Richard Treat
U.S. Department of Energy
Morgantown Energy Technology Center

W.H. Simons
West Virginia University

The results of a recent METC report describing the ranges of phy
parameters and conditions (flow velocity, magnetic field strength and
cle properties) considered favorable for wet and dry high gradient magn
separation (HGMS) and some potential uses of this technique in coal ene
related cleanup tasks is presented. These results are based upon theor
single fiber modeling of HGMS performed at METC. An overview of the ba
research which lead to this report and implications of these studies on
applicability of single and multiple fiber models of fibrous filters wh
discussed.

D. O. Johnson and J. E. Bogner

Argonne National Laboratory

This report summarizes the techniques and reagents used to control
treat mine drainage at 20 surface coal mines in the eastern and central U
Mine operations range from small contour mines to mountaintop removal ope
tions to large area mines. Of the 20 mines surveyed, 10 are or have used
chemical reagents to neutralize acid mine drainage. In the remainder,
effluent pH generally falls within the U.S. Epa limits of 6-9, and settli
ponds only are utilized to promote flocculation of suspended solids and p
cipitation of dissolved solids. Where data could be compiled, the effect
ness, problems, and costs of alternative reagents are compared and contra
Further trends in mine drainage control technology for surface coal mines
explored in light of anticipated expansions in surface coal mining and re
ly promulgated EPA effluent guidelines. Major conclusions are:

1. At the present time, mine drainage control and treatment at su
   coal mines may not reflect conscientious planning and engineer
   design work by mine operators. On the whole, control technolo
   (including reagent application) may be haphazard and periodica
   inefficient. However, there are some notable exceptions.

2. Surface mine operations favor small, efficient, and above all,
   portable application systems for neutralization reagents. Bec
   effluent discharge points at surface coal mines do not remain
   stant over long periods of time and because discharges are gen
   ally small (<5 gpm) and variable, it is not economically feasi
   for surface mine operators to install sophisticated, permanent
   treatment facilities.

3. When choosing a reagent to neutralize mine drainage, reagent c
   per unit quantity is less of a deciding factor to surface coal
   mine operators than east of reagent applications and handling.
   Thus, small caustic soda (NaOH) and soda ash (Na_2CO_3) treatmen
   systems are common, even though reagent costs (based on treati
   water of equivalent acidity) may be several times the cost of
   hydrated lime or limestone treatment.

4. There needs to be more effort on the part of surface mine oper
   for pre-mining planning to minimize pyrite oxidation and hydra
   Some additional investment in exploration plus a prudent choic
   a mine plan, drainage plan, and reclamation plan may minimize
   generation of poor quality effluents, i.e., those which are no
   compliance with EPA guidelines. Mine operators may thus reali
   long-term economic benefits from minimal initial investments t
   prevent the generation of poor quality effluents as opposed to
   maintaining treatment facilities during and after mining.

R. V. Kromrey, R. Naismith, ...

Atlantic Research Corporation

The use of coatings to prevent dust emissions and leachates from
stockpiles was studied under sponsorship of the Department of Energy, D
of Environmental Control Technology, under contract EP-78-C-02-4632. T
coatings considered included compositions formed of a filler such as pu
ized coal and a binder consisting of a combination of waxes and plastic
Various latex emulsions, both with and without fillers, were also evalu

The purpose of coal coatings is to seal the surface of the stock
This prevents water penetration into the coal. By sealing the surface
pile, dust losses are prevented and leachate formation is minimized. A
culation through the stockpile is also greatly reduced. This yields th
added benefits of reduced oxidation of the coal and prevention of sponta
ignition. Cold weather handling characteristics of the coal are also in

Physical properties of the coatings were measured. Included were
characteristics as resistance to water penetration and degradation as a
result of thermal cycling. Application techniques were also evaluated.
hot-applied and cold-applied coatings were considered.

Protective coatings appear to be an attractive means of preventic
fugitive emissions from coal stockpiles. The economic benefits from red
oxidation and improved handling more than offset the cost of application
Use of coatings on unit trains may also be attractive.

Erle C. Donaldson

U.S. Department of Energy
Bartlesville Energy Technology Center

Enhanced oil recovery processes are still in the stage of developm
The transition from pilot testing to full scale field application depends
upon a complex interaction of foreign and domestic politics and economy,
well as the success of field research that may improve the economy of enh
oil recovery processes. Underlying all development and expansion activit
associated with oil production is the constant need for protection of the
environment from pollution. However, unanswered questions regarding the
environmental consequences of enhanced oil recovery activities should be
addressed during the period of pilot field testing which is now in progre

Oil displacement by injection of brines (the waterflood process) e
the surface processing of large quantities of saline waters as the waterf
progresses creating the potential for pollution of surface waters and sha
fresh water aquifers. Improved waterflooding techniques involve the intr
duction of surface active agents (detergents), caustics, and organic poly
compounds (particularly polyacrylamide) thus producing a step increase in
potential for pollution. It is increased another step when the micellar-
polymer process is employed since the micellar solution is a mixture of
surfacant, oil, water and a cosurfactant (usually an alcohol).

Enhancement of oil production by thermal methods adds another dime
to the environmental hazards through air pollution from steam generators
the produced fluids.

Other field operations, such as drilling and renovation of wells,
create local environmental hazards but these are becoming regional concer
as the search for new oil and the reactivation of oil fields accelerates.

1. FOSSIL FUELS-PRECOMBUSTION

Coal preparation represents a double-edge sword. One edge will
reduce environmental degradation caused by sulfur dioxide emissio
and will minimize the fallout of hazardous elements such as
cadmium, arsenic and lead from stack gas fumes. The other edge,
unless blunted, will cause increased water pollution when prepara
plants discharge fine wastes into ponds and streams. Furthermore
preparation of solid wastes can produce large amounts of leachate
containing acid and also relatively high concentration of the
fugitive elements. This double-edge cause/effect relationship
has led to the of-repeated statement of substituting a water poll
problem for an air pollution problem. During the next few minutes
I intend to discuss current and planned technology developments
for mitigating air, water, and land pollution resulting from the
use of coal.

Because not everyone is familiar with the term "preparation"
perhaps a brief description is in order. Coal preparation is a
term which describes the process of changing the physical and
chemical character of run-of-mine coal to improve its utilization.
Preparation can mean no more than crushing coal to some manage-
able top size so no lumps are larger than 3 inches. At the other
extreme, preparation can involve fine grinding to minus 200 mesh,
multi-circuit cleaning to separate the liberated pyrite and
ash from coal particles, filtering or dewatering the clean coal
concentrate, drying the concentrate and finally reconstituting
the powdered coal to form briquetts or pellets to improve the
handling and transporting characteristics of the coal. Chemical
desulfurization and ion-exchange processes are also part of
the "coal preparation" process. I could go on in describing
the many ancillary processes associated with coal preparation
but this is neither the time nor the place. I merely want to
dispel the image that some of you may have that coal preparation
is little more than a breaker or crusher where coal is reduced
to manageable lumps followed by a washing tub or launder which
"cleans" the coal.

Today, coal is prepared or cleaned to remove excessive amounts of

ash-forming minerals, and to reduce the sulfur content. I don't have the composition of the average run-of-mine coal going into a preparation plant but such ROM coal may contain 20-25 percent ash and 2.5 percent sulfur. The plant product might contain 8 percent ash and 1.7 percent sulfur. As you can see from these numbers current technology falls short in meeting EPA standards on sulfur dioxide emissions and with 8 to 10 percent ash, the coal can hardly be classed as a premium quality fuel in competition with petroleum and natural gas.

This description of the state-of-the-art of coal preparation may enable you to understand the research projects underway and planned for this year.

Obviously, we should remove more of the ash than say roughly 50 percent as contained in ROM coal for economic benefits and more importantly, to reduce the quantity of fugitive elements that are re-introduced into the environment. Furthermore, more sulfur, both pyritic and organic should be removed prior to combustion.

We have a number of projects aimed at developing processes for liberating ash and pyrite from coal particles and then separating the ash and pyrite. Fine grinding with a rod or ball mill in closed circuit with a classifier appears technically feasible and economically practical but we need to demonstrate fine grinding technology and other comminution processes including chemical.

A number of unproven processes appear promising in separating liberated gangue particles from clean coal particles. Froth flotation, of course, is not unproven except more advanced procedures are required for preferentially separating pyrite. As a consequence we have several grants plus an intramural project on flotation.

Bulk oil flotation or oil agglomeration also shows great promise as a means of separating fine coal from ash particles. Unfortunate pyrite responds to oil the same as coal. Several projects are underway to alter the surface of pyrite particles in an effort to reduce their flotability.

High gradient magnetic and super conducting magnetic separators are being developed for removing paramagnetic pyrite and ash paticles from powdered coal. This technology may have application in both the wet and dry modes. DOE has several grants and contracts

chemical desulfurization processes. It's too early to predict
which processes will be pushed to a demonstration stage in the
early 1980's and perhaps the commercialization stage by the mi
1980's.

Laboratory data shows that chemical and physical desulfurizatio
are complementary processes. Coal is ground, the ash and pyrit
removed with the "clean" coal entering the chemical desulfurizi
circuit. Data is too sketchy for reliable cost estimates but I
hopeful that a combined physical and chemical process can be he
to the $15-$20 per ton range. If so, the combined physical and
chemical process would be competitive with lime/limestone and
other FGD systems.

For any process or technology involving a system of processes,
can assign certain plusses and minuses. If we believe strongly
in a program and are closely identified with it, all too often
we lose our objectivity. In my blindness, I can identify a
number of benefits resulting from pre-combustion cleanup of coal
but only one minus. Not all coals are amenable to physical and
chemical cleaning which means, for these coals, other forms of
cleanup will be required such as FGD or FBC. But there is a ra
of hope even for these refractory high sulfur coals because a
new technique has been suggested that will permit burning a
moderately high sulfur coal in conventional boilers without FGD
I have only the vaguest hint of such a combustion process but t
separate research efforts indicate that an alternative to FGD
and FBC is in the early development stage.

It's much easier to talk about the plusses or benefits of physic
and chemical cleaning in reducing environmental degradation. Th
was no attempt to list the benefits in order of importance but
everyone recognizes that reduced sulfur emmissions is natural and
Many coals can be easily and cheaply beneficiated by removing
most of the pyritic sulfur with sulfur dioxide emissions reduce
by 50 percent or more. Chemical cleaning will remove some of th
organic sulfur so sulfur emmissions are further reduced to th
percent range. Fortunately, many of the fugitive elements are
associated with either the pyrite or ash minerals so these
fugitive elements are not available for redistribution into
the air as fallout. Some of these elements, cadmium for example
if redistributed and introduced into the food chain could repres
a significant health hazard. A normal level of cadmium in ROM
coal is in the 2-5 PPB range but only 0.2 PPB in clean coal. Th
same case hold true for the elements arsenic, lead and mercury p
others.

These trace elements associated with ash and pyrite can be safely stored in carefully prepared land fills so these elements are not readily leached and redistributed in ground water. We are developing ideas for projects leading to improved waste storage methods. The waste impoundments of the kind that burst, drowning 120 people at Buffalo Creek, West Virginia, are outmoded.

Although this is a conference on environment, economics cannot be ignored so I need to say a few words about costs of coal preparation as a means of minimizing environmental degradation.

Coal preparation costs to remove sulfur and ash can vary widely depending on the complexity of the flowsheet and the processes used to recycle plant water and for solid waste disposal. A simple jigging plant may cost $2-$3 per ton of coal for combined capital and operating costs. Recent estimates run as high as $9 per ton of coal processed in complex plants which included filter pressing fine waste so it can be added to coarse waste in a compacted and impervious land fill. The $9 per ton figure is high but well below the $15-$17 per ton for flue gas scrubbing. Futhermore, a clean coal feed to a utility can result in "saving" as much a $5-$6 per ton under the cost of burning a dirty or high ash coal.

Many Eastern and Midwestern coals can be physically and chemically cleaned to meet current EPA emission standards at a combined cost in the $15-$20 range. At these costs physical and chemical cleaning is very competitive tp FGD at $15-$17 per ton because to this cost of $15-$17, a penalty of $5-$6 per ton must be added to cover the increased costs of buring ROM coal versus burning a cleaned coal. This could be shown in another way by subtracting the $5-$6 per ton of coal "benefit" from the cost of cleaning the coal. I've spent more time on the economics of cleaning coal than originally intended but it's important to understand that beneficiating coal may be preferable as a means of minimizing environmental degradation of land, water, and air, but it also has economic advantages.

INTRODUCTION

In the early nineteen seventies, public concern was aroused by the appearance of a number of newspaper and magazine articles concerning me pollution. Although most of these dealt with mercury in natural water and its effect on aquatic life, a few suggested that the burning of fo fuels might contribute significant amounts of mercury to the environmen At that time, a program was established by the coal industry through i research organization, Bituminous Coal Research, Inc., to investigate evaluate such potential problems concerning mercury and other trace el in coal and coal-related materials. An additional motive for the prog was the increasing concern with trace elements on the part of the gove regulatory agencies and the need to temper any future judgments agains coal industry with the presentation of factual information.

The first order of business in the new BCR program was the develo or adaptation of analytical procedures for the precise, accurate deter tion of trace elements in coal and coal-related materials. Some of th formation developed on the program was described in two reports (Bitum Coal Research, Inc., 1974 and 1975). Later, these analytical capabili were tested and applied to solving potential coal industry problems in ating the effect of a rough coal-cleaning process on the distribution removal of potentially harmful trace elements in coal (Ford, Care, and Bosshart, 1976). In that study, involving coal samples from only one of an extensive cleaning process specifically designed for pyrite rem some beneficiation with respect to trace elements was demonstrated eve only the initial rough cleaning.

Based on those promising results, a more extensive coal cleaning was outlined, specifically designed to evaluate the effect of such cle on trace or fugitive elements, those constituents of coal which have t potential to be released and cause environmental problems. This pape cribes initial progress on the fugitive element studies. The work was inally funded jointly by the U.S. Bureau of Mines, by the U.S. Energy and Development Administration (ERDA), and by Bituminous Coal Research Funding is presently continuing with ERDA which is now part of the U. Department of Energy.

Background and Justification

Coal has been found to contain nearly every naturally-occurring With the exceptions of carbon, hydrogen, oxygen, nitrogen, and sulfur are the principal constituents of coal, as well as iron, aluminum, si and alkaline earth metals in the ash, most elements are present in mi trace amounts.

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*Bituminous Coal Research, Inc., 350 Hochberg Road, Monroeville, PA

During coal mining, preparation, and utilization, these elements may be released to the environment. Even though these fugitive elements are normally present at extremely low levels, it may not be possible to ignore them as some are known to be harmful to plant and animal life at relatively low concentrations. The problem may, in fact, be compounded due to the large coal tonnage consumed in electric power generation and the anticipated consumption for coal conversion.

Trace elements, specifically mercury, cadmium, lead, arsenic, and selenium, have been pointed to with increasing frequency over the past several years as potential environmental pollutants. One means of controlling trace-element emissions is to remove these trace constituents prior to combustion. Those trace elements associated with the ash might be removed during the coal preparation process. A preliminary study conducted by Bituminous Coal Research, Inc., demonstrated that coal cleaning is a possible technology for controlling many of these potentially harmful constituents of coal which might be released during combustion. Based on the results of the study, more extensive coal cleaning was recommended to determine which steps in the coal-cleaning process are effective in removing fugitive elements, both the trace elements as well as the more prevalent constituents such as sulfur.

The need to better understand the fate of fugitive elements during the coal mining, preparation, and combustion processes is imperative; however, to date, few systematic studies of this nature have been undertaken. This project is an initial step in that direction.

Objectives and Scope

The overall objectives of the project are: (a) to prepare a comprehensive state-of-the-art report on the effect of coal mining, preparation, transportation, and utilization on the trace elements found in coal; (b) to determine the effect of coal cleaning on fugitive elements; and (c) to provide a description of accurate analytical methods that can be used by coal industry and commercial laboratories for determining the concentration of selected trace elements in a variety of coals. The portion of the study described here involves only the effect of coal cleaning on fugitive elements; further, only the first few of twenty coals to be cleaned for the overall study will be discussed. The other objectives are being pursued but are in an intermediate stage of development.

The objectives of this portion of the study were approached as follows:

The effect of coal cleaning on fugitive elements was evaluated by exhaustively studying samples of run-of-mine (ROM) coal obtained from various geographical locations throughout the United States. All ROM samples were subjected to controlled coal cleaning at the BCR laboratories. Each coal was crushed; the coarser fractions were subjected to heavy media separations, and the fine fraction was hydraulically classified. This cleaning is representative of that which presently exists in the industry.

Each sample produced by the coal-cleaning task was characterized
eral chemical and trace element analysis, as well as petrographic anal
where appropriate. Those fugitive elements chosen for study include t
trace elements antimony, arsenic, beryllium, cadmium, chromium, copper
rine, lead, manganese, mercury, nickel, selenium, vanadium, and zinc,
with the more prevalent constituents such as sulfur.

EXPERIMENTAL PROCEDURE

A major portion of the overall study is to determine the effect o
cleaning on fugitive elements. This portion of the study can be divid
three segments--coal cleaning, coal analysis, including petrographic a
and data evaluation. The experimental approaches to each of the three
ments are as follows:

Coal Cleaning

Approximately 450 kg (1,000 lb) of run-of-mine coal will be colle
each of twenty mines, placed in polyethylene bags to prevent trace-ele
contamination, and returned to BCR in 55-gallon drums. In each case,
coals will be representative of the seam or seams being mined at that
and have been selected on the basis of present and near-future importa
utilization.

The two basic laboratory-controlled cleaning procedures utilized
for this project are diagrammed in Figure 1, Preparation Flow Schemat
Procedure A, represented by the left portion of the schematic diagram
lates coal cleaning techniques currently being utilized by the coal i
This procedure involves basic crushing and screening to reduce the co
three fractions: (a) 31.8 x 6.35 mm (1-1/4 x 1/4 inch), (b) 6.35 mm
(1/4 inch) x 30 mesh, and (c) 30 mesh x 0. The 31.8 x 6.35-mm (1-1/4
inch) fractions and the 6.35-mm (1/4-inch) x 30-mesh fractions were t
cleaned by heavy media gravity separations (Leonard and Mitchell, 196
utilizing magnetite and the BCR double cone heavy media device pictur
Figure 2. Three separating gravities (1.35, 1.55, and 1.80) were use
ducing four gravity fractions for each of the two coarse-size fractio

The minus 30-mesh fraction was cleaned by utilizing the hydrauli
sifier shown in Figure 3 after removal of the minus 270-mesh fines.
fractions were produced from this cleaning: a low-velocity overflow
medium-velocity overflow, high velocity overflow, and a sink fractio

Figure 1. Preparation Flow Schematic
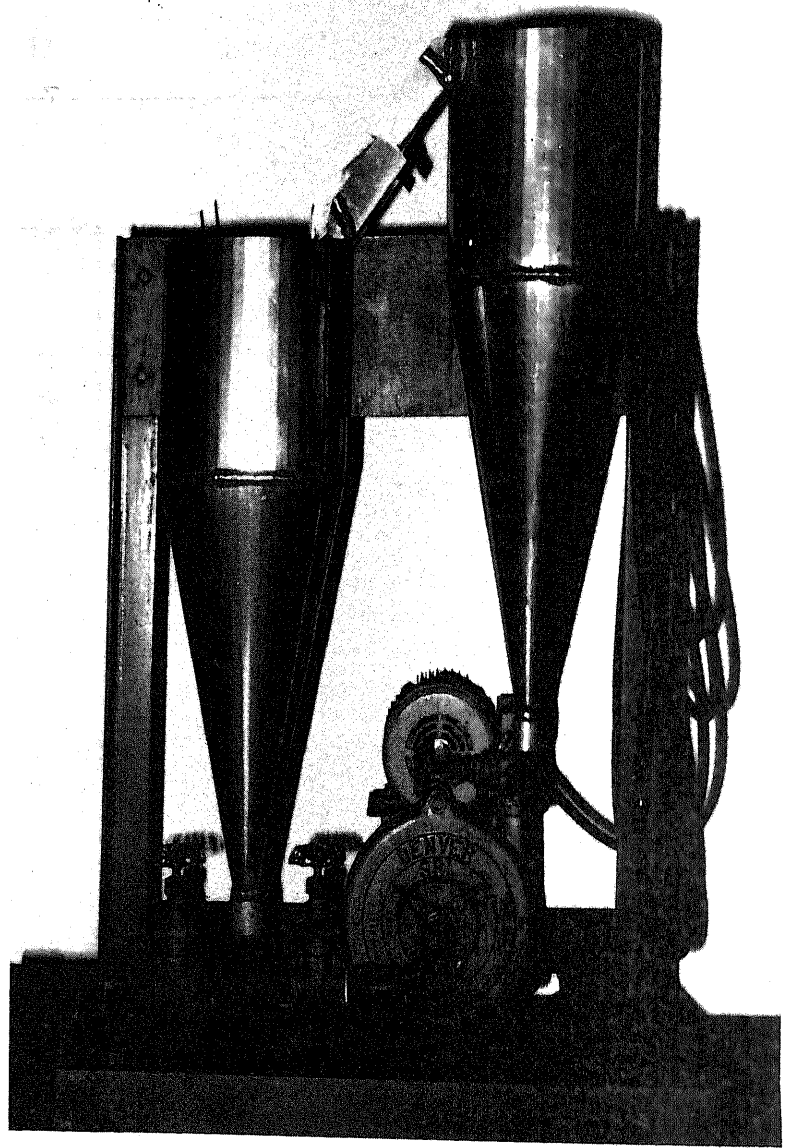
6082P21

Figure 2. Double Cone Heavy Media
Separatory Unit
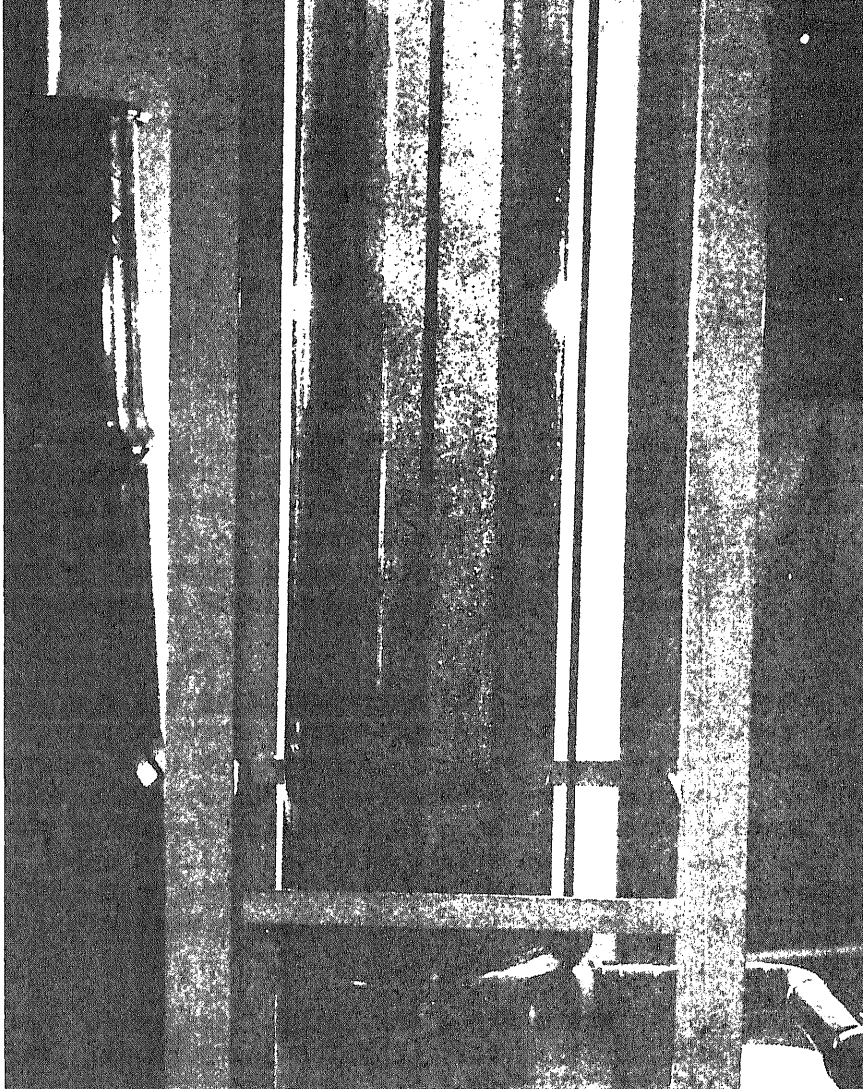
6082P7

Figure 3. Hydraulic Classifier Column

shown in Figure 1, the 31.8-mm (1-1/4-inch) x 0 ROM coal was reduced to a series of fine coal fractions using the screening apparatus shown in Figure 4. The fractions were sized from 30 mesh to minus 270 mesh and then cleaned in the hydraulic classifier. A schematic of the components of the hydraulic classifier system is shown in Figure 5. All but the minus 270-mesh fractions were subjected to hydraulic classification to produce an ultra-clean coal fraction, a clean coal fraction, a shale fraction, and a pyrite fraction for each of the size fractions. This "optimum" coal cleaning may not presently be feasible at commercial levels but was utilized in this project to identify trace elements present in fine clean coal, shale, and pyrite fractions, and to allow comparison with those found in larger-sized fractions.

By utilizing both Procedure A and B, as many as 81 samples could be generated for trace element analysis.

Analytical Methods

For a thorough evaluation of the effect of cleaning on the coals, many general chemical determinations were made as well as the petrographic and trace determinations. These included proximate analysis (moisture, ash, volatile matter, and fixed carbon), ultimate analysis (carbon, hydrogen, nitrogen, total sulfur, chlorine, and oxygen by difference), calorific value, and sulfur forms. ASTM methods (ASTM, 1977) were used whenever possible and appropriate.

The major constituents of the coal ash--including silicon, aluminum, iron, magnesium, calcium, and titanium--were determined by optical emission spectrographic (OES) techniques. Sodium and potassium were determined by atomic absorption. Phosphorus was determined either by a wet-colorimetric procedure or by atomic emission techniques utilizing apparatus purchased for this project. The atomic emission spectrometer, a multi-element, direct-reading analytical tool with a plasma excitation source, provided initial accuracy checks for phosphorus and for those elements determined by atomic absorption.

A major portion of the BCR methods for determining trace constituents in coal is based on atomic absorption for the following reasons. First, and most important, proper use of this technique has been demonstrated to result in accurate, precise concentration values for trace constituents of coal when precautions are exercised in preparing the sample for these measurements. A second reason for selecting atomic absorption is its potential use for these types of analyses by coal industry and other laboratories. While the corresponding instrumentation is by no means inexpensive, it is certainly less expensive than other more exotic, equally accurate methods. Furthermore, a skilled technician can conduct the analyses once the procedures are in an advanced state of development.

6082P16

Figure 4. Wet-Vac Screening Apparatus

City Water Supply

Water Tank 300 Gallon

Differential Pressure Gage

Water U-Tube Nanometer

Venturies

1-1/2" ID

3/4" ID

Classifier Column

Water Filter

325 Mesh Screen

To Drain

BCR 6082
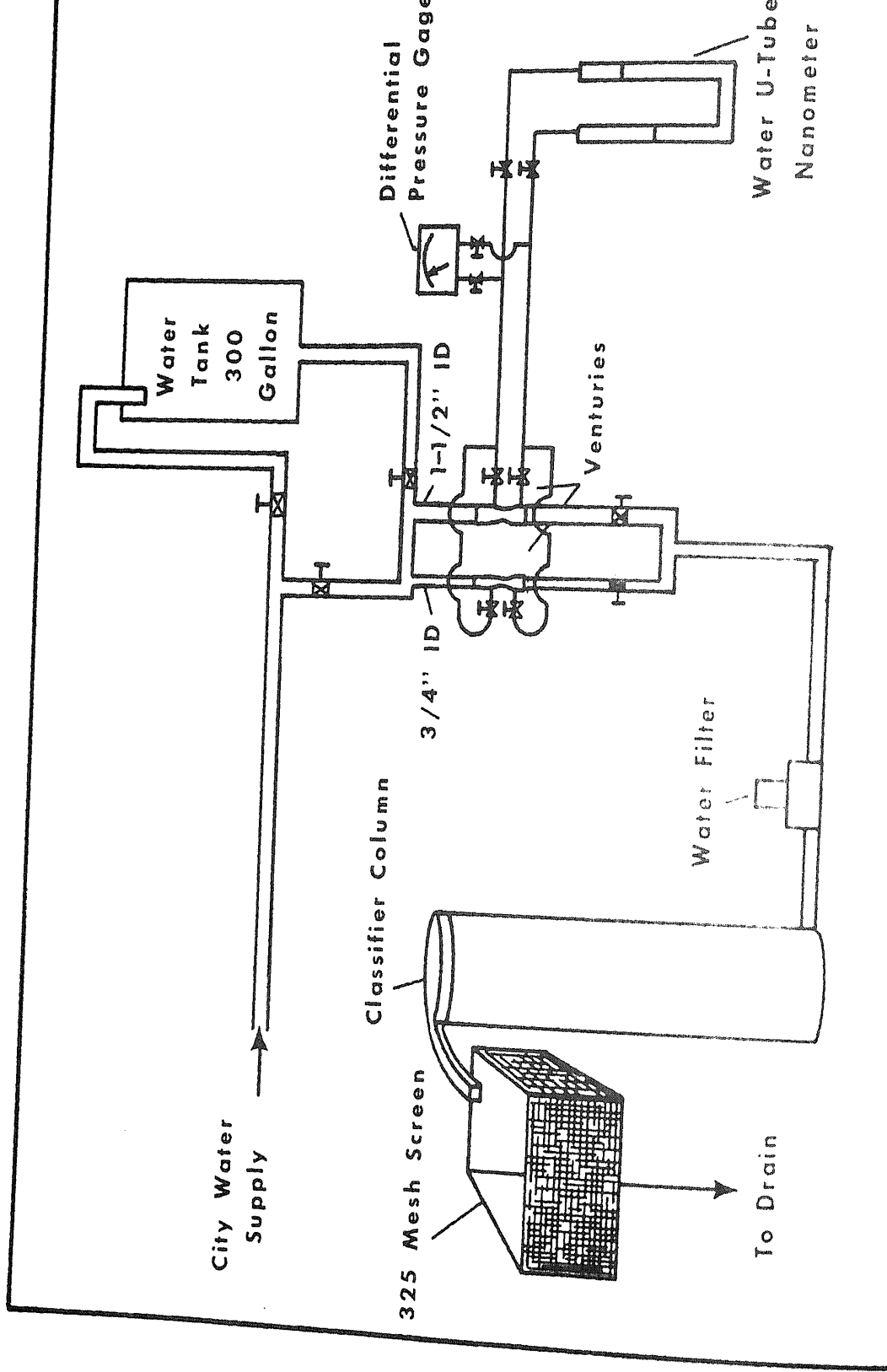
flame technique: arsenic, beryllium, chromium, copper, manganese, nickel
selenium, vanadium, zinc, antimony, sodium, and potassium. The cadmium an
lead concentrations were too low in each of these coals to be detected by
this flame technique; therefore, these elements were then determined by a
flameless graphite furnace technique utilizing apparatus specifically pur-
chased for this determination. The apparatus will also be useful for othe
low-concentration level determinations.

The solutions for flame and furnace atomic absorption as well as for
atomic emission were prepared by dissolving the ash in teflon beakers with
aqua regia/hydrofluoric acid (1:1) by boiling to dryness, adding nitric ac
and diluting to volume.

Arsenic, selenium, and antimony were determined by a unique procedur
developed at BCR based on Eschka fusion, hydride generation, and atomic
absorption using a hydrogen-argon flame. This procedure is presently bei
considered for round-robin testing by ASTM Committee D05 on Coal and Coke

Mercury was determined by a combustion bomb method developed at BCR a
by a double-gold amalgamation system constructed at BCR. Both techniques
involve flameless atomic absorption and both are being considered for roun
robin testing by ASTM Committee D05 on Coal and Coke. The first method ha
been tested with a great deal of success. Testing of the double-gold amal
gamation system has been hampered by so few of the systems being availabl

Fluorine was determined by a combustion bomb-selective ion electrode
method. As the work progresses, the analytical techniques used, particula
for the trace-element determinations, including the most recent refinement
are being written, tested, and modified where needed. Later they will be
incorporated into an analytical procedures manual for submission with the
final report for this sponsored program.

The results of analyses are displayed on data sheets developed to sh
the results of each analytical determination for each of the various frac
obtained during the cleaning. One example of these is shown as Figure 6,
which contains the ash content for all of the fractions obtained during
cleaning of coal 1R, the first coal. From the data in this figure and fr
the other similar data sheets, obvious analytical errors can be immediate
spotted. In this case, they could be observed readily as interruptions i
the trend of low to high ash content from clean coal to refuse fractions.
With the voluminous data being obtained during the course of this project
would be easy to miss such simple errors caused, perhaps, by an incorrect
recorded sample number. In one case in a previous study, each fraction o
tained had a higher concentration value than the feed from which it came.
This was traced to a dilution error during analysis. Displaying the data
in Figure 6 minimizes the chances for these kinds of errors.

The analytical results for the individual samples are displayed as i
Figure 7. The individual samples were also divided into groups for a cle

Analysis: Ash, percent

Coal: 1R

ROM
19.1

split

split

screened

1-1/4"
x 1/4"
26.8
6.22
19.2
41.6
79.4

1/4"
x 30M
15.8
5.86
22.8
55.8
78.6

screened
30 x 270M
13.0
6.57
8.47
19.4
69.2

-270M
21.1

-30M
22.3

-270M
21.8

200
x 270M
18.2
6.14
17.2
51.2
60.2

140
x 200M
19.8
5.38
16.2
52.8
65.2

-100M
21.9

100
x 140M
21.4
4.46
12.8
49.0
69.8

+100M
27.6
4.61
12.0
43.9
73.9

+30M
36.5
6.14
32.0
83.4
82.0

30
x 40M
22.8
4.22
12.5
58.2
82.3

40
x 50M
17.2
3.28
8.68
45.5
79.8

50
x 70M
15.6
3.22
8.75
39.0
76.0

70
x 100M
16.9
3.57
9.64
44.5
70.0

100
x 140M
17.2
4.16
11.4
45.5
66.3

140
x 200M
19.9
4.76
12.4
50.2
64.6

200
x 270M
21.2
4.73
14.4
47.5
55.4

-270M
31.4

Analytical Lab No: 77-1071   Sample Code No: 1R-3M-2HC

PROXIMATE, %		ELEMENT, ppm	
Moisture	0.64	Arsenic	15.8
Ash	8.47	Beryllium	1.34
Volatile Matter	32.8	Cadmium	0.045
Fixed Carbon	58.7	Chromium	16.3
ULTIMATE, %		Copper	13.7
Carbon	78.4	Fluorine	65.9
Hydrogen	5.20	Lead	6.64
Nitrogen	1.44	Manganese	21.1
Sulfur	1.48	Mercury (ppb)	384
Chlorine	0.20	Nickel	14.1
Oxygen	4.81	Selenium	3.08
SULFUR FORMS, %		Vanadium	30.4
Sulfate	0.00	Zinc	19.9
Pyritic	0.91	Antimony	0.94
Organic	0.57		

MISCELLANEOUS

Calorific Value
Btu/lb   13,934

MAJORS IN ASH, %				
SiO_2	45.4		Silicon	18,200
Al_2O_3	25.7		Aluminum	11,700
Fe_2O_3	16.0		Iron	9,620
MgO	0.86		Magnesium	450
CaO	5.82		Calcium	3,580
TiO_2	1.38		Titanium	711
MnO			Manganese	
Na_2O			Sodium	135
K_2O			Potassium	1,490
SO_3	1.52			
P_2O_5	0.56		Phosphorus	210

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Figure 7. Data Sheet - Coal Preparation -

Details of each of the twenty coals have been cleaned and analyzed. At that time, the ... tion of the final report will describe the analytical procedures and ... development in sufficient detail for use by coal industry and other ... tories involved in similar work.

Petrographic Methods

Petrographic analyses were employed to supplement the chemical ... designed to characterize coal separates evolved from the gravity cle... and sizing techniques. These analyses involve the use of a light m... to identify and measure coal constituents and included impurities w... up each separate. The following analyses were used to optically cha... each sample:

Coal composition: To identify and quantify the organic consti... ents characterizing the subject separate.

Pyrite mode of occurence: To determine the relative associati... of the pyrite impurity with the coal. (Free, surface, or encased)

Pyrite size: To measure and quantify the mean projected area ... eter of the pyrite associated with the coal.

Results of the petrographic analyses will not be discussed in ... brief paper.

Data Evaluation

Further evaluation of the data was aided by use of a computer. ... balances were calculated and concentrations of the products were de... (a) based on the ultra-clean and clean coal fractions No. 1 and 2; ... on the ultra-clean and clean coal as well as the non-pyrite refuse ... No. 1, 2, and 3; and (c) based on the middlings fractions No. 2 an... might, in a real situation, be subjected to additional cleaning. ... of the computer printout for the program written for the mass bala... culations is presented in Table 1. A differential value between t... and composite is also calculated and displayed in order that judgm... be made on the entire operation including the cleaning and analyse...

Most of these calculated values might not be needed to evalua... coal and each group; however, they will be available and are easie... while the data are first being entered into the computer rather th... to reenter all of the data at some later time. For one coal, the ... balances for 37 constituents and 18 different groups of feeds and ... fractions could result in a total of almost 700 sets of individual ... tions, such as that displayed in Table 1, available for evaluation...

Analysis: Coal:

Groups

ROM

split

split

split

1-1/4" 1/4"
x 1/4" x 30M

screened
30 x 270M -270M

-100M

-30M

-270M

100
x 140M

140
x 200M

200
x 270M

140
x 200M

200
x 270M

70
x 100M

50
x 70M

40
x 50M

30
x 40M

+30M

100
x 140M

140
x 200M

200
x 270M

+100M

I

V

VI

XI

II

III

IV

VII

VIII

IX

X

XII

XIII

XIV

XV

XVI

XVII

XVIII

XIX
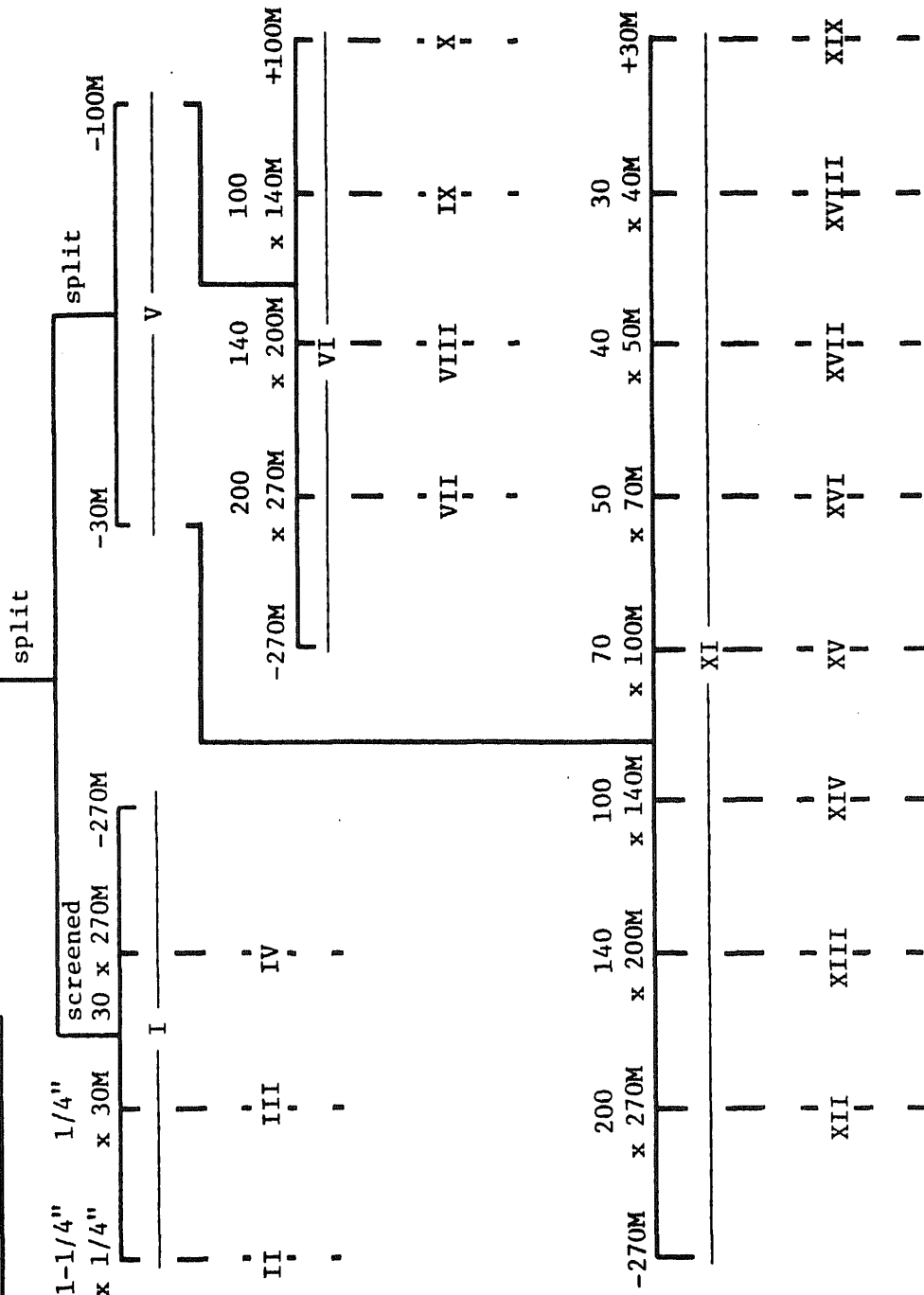
TABLE 1. SAMPLE PRINTOUT FROM MASS BALANCE CALCULATION PROGRAM

FRACTION NUMBER	WEIGHT FRACTION	SULFUR CONCENTRATION		WEIGHTED CONCENTRATION
1	0.574	1.09	=	0.626
2	0.155	1.76	=	0.273
3	0.055	3.80	=	0.209
4	0.216	3.58	=	0.773
	1.000			1.881

[C] IN FEED = 1.76

[C] IN CLEANED COAL = 1.232

*[C] IN CLEANED COAL = 1.413

[C] IN MIDDLINGS = 2.294

[C] IN REFUSE = 3.625

(COMP.-FEED) DIFFERENTIAL = 6.9%

% REMOVED = 52.228

*% REMOVED = 41.116

*% YIELD = 78.400

% YIELD = 72.900

to demonstrate the relationships between the percent removed of each cons
uent with the percent removed of every other constituent. This was done
an additional means of comparing the effectiveness of the fugitive elemen
removal of the two coals. At this time, the percent removed was selected
as the parameter to be evaluated. Later, when data for more coals are av
able, relationships between concentrations will be examined more thorough

RESULTS AND DISCUSSION

Cleaning, analyses, and data evaluation of two coals are complete.
coal is a mixture of Upper and Lower Freeport seams and the other an Illi
No. 6 seam. Work on additional coals is in progress. The data were used
evaluating the effect of such cleaning on fugitive elements.

Coal Sampling

A list of the twenty coal seams to be sampled is shown in Table 2.
of these have already been acquired and are available to the project.

Coal Cleaning

The first three coals were extensively cleaned using both Procedure
and Procedure B; the fourth coal involved only the shorter Procedure A.
the weight percent, ash, total sulfur, and calorific value data for the f
two coals, the cleaning strategies employed were particularly effective a
the separations needed to attain the objectives of the project were being
achieved.

Washability studies were utilized primarily to determine how much co
could be produced at a given specific gravity and to define the ash and s
fur characteristics of the coal at that gravity. A washability study was
made by testing coal samples at carefully controlled specific gravities,
analyzing the specific gravity fractions for ash and sulfur contents. A
table was developed detailing the weight percentages and the ash and sulf
analysis for each fraction. The data were then mathematically combined i
"cumulative float" and "cumulative sink" for both ash and sulfur and were
utilized to develop "washability curves" which helped to characterize the
coal. One example of the washability tables developed for this study, th
one for the first coal, is presented in Table 3. The tables detail the s
aration gravities, the corresponding weight percentages, and the ash and
sulfur analyses for each of the three size fractions.

The washability curves for the 31.8 x 6.35-mm (1-1/4 x 1/4-inch) fra
tion of coal 1R which was cleaned utilizing the heavy media unit are show
in Figure 9. Five curves are plotted on the chart: cumulative float ash
(CFA), cumulative float sulfur (CFS), cumulative sink ash (CSA), cumulati
sink sulfur (CSS), and the yield curve. As stated previously, these curv
can be used to determine how much coal may be produced at a given specifi

TABLE 2.   COALS TO BE USED IN BCR FUGITIVE ELEMENT STUDY

Sample	Seam	Sample	Seam
1	Upper/Lower Freeport	11	Pocahontas No. 3
2	Illinois No. 6	12	Stockton
3	Rosebud	13	Sewell
4	Beulah-Zap	14	Mary Lee
5	Hannah No. 60	15	Kentucky No. 9
6	Adaville No. 1	16	Illinois No. 5
7	Castle Gate B	17	Imboden
8	Lower Kittaning	18	Upper Elkhorn
9	Pittsburgh	19	Pittsburgh
10	Meigs Creek	20	Lower Kittaning

TABLE 3. WASHABILITY ANALYSIS OF COAL 1R

Specific Gravity		Separates, percent			Cumulative Recovery, percent			Cumulative Re[covery]	
Sink	Float	Yield	Ash	Sulfur	Yield	Ash	Sulfur	Yield	As[h]
		Group II 1-1/4 x 1/4 Inch Heavy Media - coarse							
	1.35	57.4	6.2	1.09	57.4	6.2	1.09	100.0	26
1.35	1.55	15.5	19.2	1.76	72.9	9.0	1.23	42.6	52
1.55	1.80	5.5	41.6	3.80	78.4	11.3	1.41	27.1	71
1.80		21.6	79.4	3.58	100.0	26.0	1.90	21.6	79
		Group III 1/4 Inch x 30 Mesh Heavy Media - fine							
	1.35	79.6	5.9	1.06	79.6	5.9	1.06	100.0	15
1.35	1.55	6.8	22.8	2.64	86.4	7.2	1.19	20.4	54
1.55	1.80	5.2	55.8	5.67	91.6	10.0	1.44	13.6	69
1.80		8.4	78.6	11.0	100.0	15.7	2.24	8.4	78
		Group IV 30 x 270 Mesh Hydraulic Classifier							
	1.35	31.9	6.6	1.06	31.9	6.6	1.06	100.0	12
1.35	1.55	47.6	8.5	1.48	79.5	7.7	1.31	68.1	15
1.55	1.80	14.9	19.4	2.90	94.4	9.6	1.56	20.5	33
1.80		5.6	69.2	14.5	100.0	12.9	2.29	5.6	69
Average									
	1.27								
	1.31								
	1.42								
	2.46								

Figure 9. Washability Curves for the 1¼ × ¼ Inch
Fractions of Coal 1R

gravity.

By referring to Figure 9, it can be seen that if a 1.55 specific grav-
ity were chosen for the cleaning gravity of the 31.8 x 6.35-mm (1-1/4 x 1/4
inch) fraction of coal 1R, the following results would be expected: the
yield in the float fraction would be 72.9 percent of the total feed coal,
the float fraction would contain 9 percent ash and 1.23 percent sulfur, the
sink fraction would contain 71.7 percent ash and 3.6 percent sulfur. It
should also be noted that the slope of the cumulative float curves gives a
quick estimate of the difficulty of cleaning a coal. The greater the slope
the more near-gravity material and the more difficult the coal is to clean.

By interpreting the data presented and by utilizing the washability
curves, general statements can be made about the characteristics of the two
coals and the response of the coals to cleaning.

For example, it can be inferred that coal 2R is more resistant to pul-
verization than 1R. Coal 2R contains a higher percentage of material in th
coarse size fraction, 31.8 x 6.35-mm (1-1/4 x 1/4-inch), and a lower per-
centage in the fines, 30 x 270-mesh, than coal 1R. The higher percentage i
the coarse screen fraction of coal 2R indicates that less degradation oc-
curred during the screening, implying that coal 2R is harder than 1R.

When compared at a 1.45 specific gravity, the 6.35-mm (1/4-inch) x 30-
mesh fraction showed the best ash reduction potential for both coals. The
31.8 x 6.35-mm (1-1/4 x 1/4-inch) fraction of coal 1R had the highest per-
centage ash reduction (72 percent), but the feed ash was much higher than
in the 6.35-mm (1/4-inch) x 30-mesh fraction, which yielded a higher float
ash even with the 72 percent reduction. The ash reduction potential at the
1.45 gravity was poor for both coals at the 30 x 270-mesh size range. From
the washability curves, a lower specific gravity separation for the 30 x
270-mesh fractions would yield a better cleaning response.

Coal 1R showed better total sulfur reduction potentials than 2R for al
size ranges at the 1.45 specific gravity. Coal 1R inherently has a lower
sulfur content at the run-of-mine level and also proved, even for the 30 x
270-mesh fraction, to be easier to clean to an acceptable sulfur level.

The changes in the Btu levels between the raw coals and the coals wash
at 1.45 gravity were not significant. Only the 31.8 x 6.35-mm (1-1/4 x 1/4
inch) fraction of coal 1R showed a reasonable increase, 22.9 percent. The
fine fractions, 30 x 270-mesh, of both coals showed a large reduction in
Btu's when cleaned at 1.45 gravity. Again, a specific gravity lower than
1.45 would show a better response for the fines of both coals.

study are presented in Table 4. Differences in concentrations [...]
the four are apparent. For example, the average concentration f[...]
the trace elements for coal 1R is 27 ppm; for coal 2R, it is 25 [...]
coal 3R, it is 15 ppm. For the lignite, coal 4R, the average con[...]
for the same 14 elements is only 8 ppm.

Thirty-eight constituents of samples of each of the first fo[...]
coals, including the run-of-mine sample, were determined. Conta[...]
samples was a continuing problem throughout the study. Instances [...]
chromium, copper, lead, nickel, and zinc contamination were iden[...]
documented. These will be described thoroughly both in a forthco[...]
and in a report on analytical procedures. Contamination was hel[...]
mum by routinely analyzing reagent blanks and other material use[...]
project such as the magnetite used in the heavy media separations[...]

Every determination was done in duplicate. Lack of duplicat[...]
immediately precipitated an additional determination. Whenever p[...]
as time allowed, more than one procedure was used for the trace [...]
terminations as a check on the accuracy of the analytical values [...]

Finally, as a continual check on the analytical procedures d[...]
project, National Bureau of Standards (NBS) certified reference m[...]
SRM-1632 Coal and SRM-1633 Fly Ash, were analyzed along with each[...]
of-mine coal and its cleaned fractions. One example of the type [...]
ment normally obtained between the determined values and the NBS [...]
values is presented in Table 5.

A more thorough description of the analytical procedures and [...]
precision and accuracy studies is programmed at the end of the pr[...]
funded portion of this program, when the twenty coals have been c[...]
analyzed and the effect of the cleaning on fugitive elements has [...]
mined.

Mass Balance Calculations

The analytical data for each coal were used in calculating ma[...]
for the various individual cleaning schemes for each coal. The m[...]
for each of the determined constituents were calculated: (a) to [...]
integrity of the cleaned fractions and the validity of the analyt[...]
by comparing the summation of the materials in each fraction with[...]
material, and (b) to evaluate the reduction or enrichment of each[...]
ent as a result of the cleaning process.

For each constituent, the concentration determined in a parti[...]
rated fraction was multiplied by the weight fraction of the feed [...]
reported to that zone. The weighted concentrations thus obtained[...]

TABLE 4. COMPARISON OF CONCENTRATIONS OF RUN-OF-MINE
COALS 1R, 2R, 3R, AND 4R (dry coal basis)

	Coal 1R	Coal 2R	Coal 3R	Coal 4R
Ash, percent	22.3	16.0	15.8	11.0
Total Sulfur, percent	2.30	2.73	1.18	0.89
Chlorine, percent	0.12	0.33	0.01	0.07
Pyritic Sulfur, percent	1.78	2.01	1.02	0.73
Organic Sulfur, percent	0.46	0.50	0.14	0.10
Arsenic, ppm	40.2	11.0	8.54	10.4
Beryllium, ppm	1.84	1.10	0.87	0.70
Cadmium, ppm	0.08	0.47	0.12	0.06
Chromium, ppm	29.7	21.1	8.21	5.16
Copper, ppm	22.1	11.0	13.2	6.98
Fluorine, ppm	115	113	63.6	32.0
Lead, ppm	15.4	21.8	12.8	1.86
Manganese, ppm	50.0	36.8	65.2	33.4
Mercury, ppb	662	154	154	110
Nickel, ppm	20.9	18.4	4.98	4.60
Selenium, ppm	6.20	1.83	1.61	0.96
Vanadium, ppm	44.4	26.2	14.0	10.8
Zinc, ppm	35.5	91.8	12.8	3.48
Antimony, ppm	1.09	0.40	1.78	0.55
Sodium, ppm	448	1,230	248	6,630
Potassium, ppm	5,460	2,980	1,110	574
Silicon, ppm	57,800	37,900	39,800	14,500
Aluminum, ppm	30,800	17,700	20,200	6,470
Iron, ppm	21,100	19,100	8,560	7,840
Magnesium, ppm	1,360	870	3,150	4,060
Calcium, ppm	2,090	3,110	6,790	16,100
Titanium, ppm	1,670	1,010	1,090	370
Phosphorus, ppm	260	160	85	140
Calorific Value, Btu/lb	11,640	11,902	10,990	10,558

TABLE 5. COMPARISON OF TRACE ELEMENT CONCENTRATIONS
IN SRM-1632 COAL WITH NBS CERTIFIED VALUES
(All values in ppm on a dry coal basis)

Element	Average ppm Determined	NBS Value, ppm
Antimony	3.47*	not certified
Arsenic	6.22	5.9 ± 0.6
Beryllium	1.63	1.5[†]
Cadmium	0.17	0.19 ± 0.03
Chromium	20.5	20.2 ± 0.5
Copper	17.7	18 ± 2
Lead	31.7	30 ± 9
Manganese	45.6	40 ± 3
Nickel	14.1	15 ± 1
Potassium	2,680*	not certified
Selenium	2.88	2.9 ± 0.3
Sodium	362*	not certified
Vanadium	36.4	35 ± 3
Zinc	41.6	37 ± 4

* In agreement with other published values.

† Informational value.

the concentration in the feed.

The differential between composite and feed **was** obtained from each mas
balance calculation as follows:

$$\text{Differential} = \frac{\text{Composite Value} - \text{Feed Value}}{\text{Feed Value}} \times 100$$

These values, since they indicate the extent of agreement between feed and
product constituents, can offer much insight into both the cleaning and the
analytical study. Judgments are possible on the cleaning process based on
the agreement of many of the constituents within any one cleaning operation
Poor agreement generally might indicate problems with the integrity of the
samples obtained by cleaning; good agreement with the exception of one or
two constituents, might indicate problems in the analytical determination
of the constituents. A consistent positive or negative bias would indicate
gain or loss of a constituent during cleaning or analysis, or analytical
problems with certain of the fractions, perhaps the clean coal or (more
likely) the refuse.

The average percent differentials for each of the first four coals are
summarized in Table 6. The values presented in the table are the averages
(absolute value) from as many as 18 values from the individual cleaning op-
erations. Low values indicate good agreement between composite and feed.
Obviously, there is a great deal of satisfaction with these values. For th
most part, the agreement was better for coals 1R, 2R, and 3R than it was fo
coal 4R.

Some of the lack of agreement can be attributed to the low concentra-
tions of trace constituents associated with this fourth coal. The concen-
trations in solution were often at or near the detection limits of the
analytical methods. Additionally, slight contamination of trace constituen
routinely experienced and tolerated in previous analyses exerted a greater
influence on results at the low concentration levels. Such low concentrati
levels will probably be experienced with other coals for this project.

Effect of Cleaning on Distribution and Removal

The analytical data were used in evaluating the effect of cleaning the
run-of-mine coals on fugitive element removal. An example of the type of
data available, a summary of the percent of each constituent removed as a
result of cleaning coal 1R, is presented in Table 7.

This calculation assumes the first two fractions as the cleaned coal a
the last two as the refuse. The corresponding product recovery for each
group is presented at the top of each column in this table. Most of the co
stituents which were concentrated, not removed, by the cleaning were not in
cluded in this table. For the most part, these were inherent parts of the

Ash	2	3	5
Volatile Matter	2	1	1
Fixed Carbon	1	1	1
Carbon	1	1	1
Hydrogen	2	3	3
Nitrogen	2	2	5
Total Sulfur	4	2	5
Chlorine	11	6	19
Pyritic Sulfur	5	3	7
Organic Sulfur	5	3	11
Calorific Value	1	1	1
Arsenic	15	8	11
Beryllium	4	3	5
Cadmium	14	21	9
Chromiun	3	8	7
Copper	14	17	8
Fluorine	9	7	6
Lead	14	14	9
Manganese	3	7	4
Mercury	13	61	18
Nickel	9	8	25
Selenium	6	15	7
Vanadium	5	5	3
Zinc	6	21	23
Antimony	8	12	11
Sodium	10	11	10
Potassium	8	4	4
Silicon	4	4	4
Aluminum	4	4	3
Iron	5	5	9
Magnesium	7	4	11
Calcium	7	7	12
Titanium	3	4	5
Phosphorus	6	11	4
Average	6	9	8

Constituent	GROUP															
	II	III	IV	XII	XIII	XIV	XV	**XVI**	XVII	XVIII	XIX	VII	VIII	IX	X	Av.
						Product Recovery, percent										
	<u>73</u>	<u>86</u>	<u>80</u>	<u>71</u>	<u>76</u>	<u>79</u>	<u>80</u>	<u>83</u>	<u>81</u>	<u>76</u>	<u>69</u>	<u>82</u>	<u>82</u>	<u>75</u>	<u>63</u>	<u>77</u>
Ash	75	60	52	73	69	67	70	66	70	73	71	52	55	71	81	67
S_T	52	54	54	78	71	65	66	60	62	66	76	68	63	72	82	66
Cl	8	4	15	14	11	11	7	5	6	8	8	8	7	10	13	9
S_{pyr}	65	69	66	89	83	79	82	78	80	81	86	80	78	85	91	79
S_{org}	10	6	15	18	14	13	12	7	8	8	10	11	10	13	26	12
As	82	79	71	92	88	88	91	86	89	88	93	87	86	93	97	87
Be	45	22	26	38	37	28	29	26	29	38	44	23	25	37	50	33
Cd	63	53	52	64	68	63	66	63	78	67	69	58	56	66	78	64
Cr	64	41	34	51	48	45	50	46	51	56	60	35	39	55	65	49
Cu	61	50	48	66	63	57	61	55	58	64	64	49	48	64	76	59
F	61	42	42	55	56	53	56	43	51	55	61	30	31	49	67	50
Pb	71	62	59	71	70	72	73	73	75	81	65	60	66	82	88	71
Mn	89	77	58	85	83	82	85	81	85	87	82	69	75	87	93	81
Hg	55	67	69	73	72	71	65	71	70	76	82	68	64	59	92	70
Ni	53	42	42	60	58	64	55	45	50	61	64	46	49	60	72	55
Se	44	65	67	82	78	73	75	74	72	79	83	74	72	80	88	74
V	63	36	31	47	39	41	42	39	44	55	58	30	32	52	66	45
Zn	74	58	45	71	66	61	66	62	65	71	65	51	51	67	78	63
Sb	29	33	28	36	42	30	35	22	32	28	52	28	29	41	60	35
Na	73	46	45	66	61	56	61	56	61	65	64	42	46	62	73	58
K	80	67	55	73	69	53	72	69	74	78	72	49	54	73	83	68
Si	77	61	51	72	68	67	69	68	71	74	71	49	54	71	80	67
Al	69	52	46	65	60	59	61	58	62	68	64	42	47	63	73	59
Fe	73	72	67	91	85	84	86	83	84	87	87	82	78	90	94	83
Mg	85	67	52	72	69	70	73	72	77	84	75	48	55	74	84	70
Ca	53	42	38	77	76	69	67	58	58	59	62	59	59	68	76	61
Ti	68	49	42	59	56	52	55	52	58	64	62	43	42	60	71	56
P	46	24	34	51	44	38	43	37	31	43	53	33	35	45	61	41
Average	60	50	47	63	61	58	60	56	59	63	64	49	50	62	74	58

*Cleaned Coal = Fractions 1 and 2

percent minus the average product rec̲o̲v̲e̲r̲y̲ ... ...
sult was a slight concentration of these two in the cleaned coal ove
amounts in the feed.

The averages by group and by constituent reflect generally good
of most of the constituents. Arsenic, iron, manganese, pyritic sulf
nium, lead, mercury, and magnesium were removed most effectively. B
antimony, phosphorus, and vanadium were removed least effectively.
and organic sulfur were actually concentrated slightly in the cleane

Similar data are available for each coal, assuming either the fi
or first three fractions from the heavy media or the hydraulic classi
separations as the cleaned coal. The data are further summarized, in T
by constituent for the first four coals. The values presented in Tal
are the averages from the individual values for each of the cleaning
tions, for example, from the last column on the right in Table 7.

The differences in the effectiveness of cleaning each coal can r
be seen from the data in Table 8. Most constituents were removed mor
fectively from coal 1R than from the other coals, but the product rec
was also the lowest for this coal. Cleaning was least effective witl
4R, the lignite. However, the principal reason for this is simply tl
concentrations of the impurities in this coal, as previously displaye
Table 4, were relatively low prior to cleaning.

It must be pointed out at the same time that the calorific value
coal was also the lowest of the four. Perhaps the concept of a calco
expression relating the concentration of impurities per calorific val
ilar to the "pounds of sulfur per million Btu's," is needed to compar
trace impurities in a wide variety of coals on an equal basis.

Differences in the relative rates of removal for each coal can a
observed from the data in Table 8. Cadmium and zinc were removed mor
tively from coal 2R than from the others. They were also present in
concentrations in this coal from the Illinois basin than in the other

Linear correlation coefficients and F-test ratios were calculate
the constituents to demonstrate the relationships between the percent
of each constituent with the percent removed of every other constitue
relationships were evaluated among "percent" of the constituents remo
group rather than among "concentration" of each constituent removed b
This was done simply because two coals are not a statistically signif
representation to permit drawing any specific conclusions concerning
general and the effect of cleaning them on fugitive element removal.
tration data will prove more meaningful later in the study when more
are cleaned.

Product Recovery	77	87	87	88
Btu Recovery	91	97	92	94
Ash	67	48	41	23
Total Sulfur	66	46	56	46
Chlorine	9	8	16	14
Pyritic Sulfur	79	55	61	50
Organic Sulfur	12	9	16	14
Arsenic	87	53	70	50
Beryllium	33	20	21	14
Cadmium	64	77	34	15
Chromium	49	28	29	24
Copper	59	37	28	18
Fluorine	50	33	26	12
Lead	71	61	31	22
Manganese	81	65	20	33
Mercury	70	42	41	31
Nickel	55	25	27	19
Selenium	74	34	45	24
Vanadium	45	23	25	16
Zinc	63	71	30	22
Antimony	35	19	22	19
Sodium	58	25	28	9
Potassium	68	39	53	19
Silicon	67	43	43	32
Aluminum	59	42	37	19
Iron	83	65	76	51
Magnesium	70	42	13	12
Calcium	61	72	14	16
Titanium	56	34	33	27
Phosphorus	41	66	21	14
Average	58	42	34	24

The F-statistic was then utilized in evaluating the relationship at the selected confidence level. The relationships are summarized Table 9 for the first two coals. Only those having the highest degr of correlation are listed. Even with the imperfect means of evaluat the distinct differences between the two coals, particularly in resp to cleaning, are again evident. The associations for 2R are essenti those described previously and proficiently for Illinois coals (Ruch

relationships between the [text cut off]

These studies with the first few coals, as well as previous li[text cut off]
cleaning studies at BCR with eight coals have confirmed that remova[text cut off]
potentially harm ul trace elements can be effected by coal cleaning[text cut off]
studies thus far with the coals reported here revealed differing re[text cut off]
to the various cleaning processes. Generalizations concerning the [text cut off]
cleaning on fugitive elements are not possible at this time. Speci[text cut off]
sions concerning elemental distributions are not possible either at[text cut off]
Some trends have already been noted and these will be reexamined wh[text cut off]
statistically significant number of coals have been cleaned and aña[text cut off]
Studies with additional coals are planned and already under way.

The program is flexibly designed to add or delete constituents[text cut off]
by mutual agreement between the sponsor and BCR, as a result of new[text cut off]
legislation, or by some new evidence of environmental contamination[text cut off]
extensive cleaning scheme will also be similarly modified when warra[text cut off]
the initial results of the studies. Milestones in reporting for th[text cut off]
include a report in preparation on the state-of-the-art of fugitive[text cut off]
emissions as they relate to the coal industry, as well as two final[text cut off]
one describing the results of the studies, the other including a co[text cut off]
description of the analytical procedures used in the study.

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		S_{org}
Ash	Cr, Cu, F, Mn, Zn, Na, Si, Al, Mg, Ti	K, Si, Al, Mg
S_T	S_{pyr}	S_{pyr}, Fe
Cl		S_{org}
S_{pyr}	S_T, As	S_T, Pb, Fe
S_{org}		P.R.*, Cl
As	S_{pyr}, Fe	
Be	P.R.*, Cr, V, Na, Ti, P	V, Ti
Cd		Zn
Cr	Ash, Be, V, Zn, Na, Si, Al, Mg, Ti	V
Cu	Ash, Zn, Na, Al, Ti	
F	Ash, Na, Al, Ti	K, Si, Mg
Pb		S_{pyr}, Fe
Mn	Ash, Zn, Si, Al	Ca
Hg		
Ni		
Se		
V	Be, Cr, Na, Al, Ti	Be, Cr, Ti
Zn	Ash, Cr, Cu, Mn, Na, K, Si, Al, Mg, Ti	Cd
Sb		
Na	Ash, Be, Cr, Cu, F, V, Zn, Si, Al, Mg, Ti	
K	Zn, Si, Al, Mg, Ti	Ash, Si, Mg, P
Si	Ash, Cr, Mn, Zn, Na, K, Al, Mg, Ti	Ash, F, K, Al, Mg
Al	Ash, Cr, Cu, F, Mn, V, Zn, Na, K, Si, Mg, Ti	Ash, Si
Fe	S_{pyr}, As	S_T, S_{pyr}, Pb
Mg	Ash, Cr, Mn, Zn, Na, K Si, Al, Ti	Ash, F, K, Si
Ca		Mn
Ti	Ash, Be, Cr, Cu, F, V, Zn, Na, K, Si, Al, Mg	Be, V
P	P.R.*, Be	K

*P.R. = Product Recovery

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ABSTRACT

The aqueous drainage from coal piles and coal refuse dumps frequen~
taminated with acids and a variety of trace elements and inorganic
The Los Alamos Scientific Laboratory is conducting research, joint
by DOE/ECT and EPA, to assess the nature and magnitude of trace e
drainage from coals and coal preparation wastes, to identify the
of environmental concern in these effluents, and to define necess~
mental control technology for this form of environmental pollutio~
emphasis of this program is on the laboratory assessment of enviro
trol options for the drainages from high sulfur coals and coal wa~
presentation will review some of the accomplishments of this rese~
to date, and discuss the various drainage control options availab~
industry.

INTRODUCTION

It has been well established that the drainage from coal refuse d
highly contaminated with trace or inorganic elements; however, l
about the quantities of undesirable elements that are released in
ronment from this source.[1] Development of the necessary control
for human and environmental protection requires quantitative eval
extent and severity of the problem. LASL has been directed by DO
assess the nature and magnitude of the trace elements in the drai
preparation wastes, to identify the trace elements of greatest en
concern in these materials, and to evaluate required pollution co
gy for this form of environmental contamination.

The research in this program is being conducted in several phases
phase included studies of the structure and weathering and leachi
of the trace elements in selected samples of high sulfur refuse a
These investigations established the overall potential of these m
cause trace element contamination, and revealed the identities of
trace elements of concern in the refuse and coal pile effluents.
ion gathered on refuse and coal structure and environmental behav
the basis for the present phase of the program, which involves as
development of control technology to lessen the environmental imp
element pollution of coal or refuse associated waters.

Research has now been started to identify suitable means to contr
ment contamination of the drainages from high sulfur coal prepara
These control techniques can be roughly divided into three catego
immobilization or removal of contaminants prior to disposal of th

EXPERIMENTAL

The coal preparation wastes used in this work were collected from three coal cleaning plants (designated Plants A, B and C) in the Illinois Basin. These samples of high sulfur coal refuse are typical of the wastes produced by cleaning of the major coal types currently mined in the region.[2]

Both static and dynamic leaching experiments were conducted to evaluate the behavior of the trace elements in the Illinois Basin coal wastes under simulated environmental conditions and to test the effectiveness of potential environmental control methods. The static experiments were carried out by agitating known quantity of crushed refuse or composite (50 g) in the presence of a constant volume of distilled water (200 mℓ) for varying periods of time. In the dynamic or column leaching tests, a crushed sample ($\sim$ 1500 g) was packed into 70-cm-long by 4.6-cm-diam glass column and distilled water was continuously monitored through the column at a rate of 0.5 mℓ/min. The elemental compositions of the experimental leachates were determined by neutron activation analyses, atomic absorption spectrophotometry, optical emission spectroscopy and wet chemical methods.[2,3]

RESULTS AND DISCUSSION

Static and dynamic leaching experiments were performed to evaluate the trace element behavior of Illinois Basin coal wastes under simulated weathering conditions. These experiments were done to provide information needed to predict quantitatively the trace element levels in the drainage from coal refuse dumps or disposal areas and to identify those elements of environmental concern.

Perhaps the single most important characteristic of the high sulfur refuse materials during aqueous leaching is their pronounced tendency to rapidly produce acidic leachates. This is due to the oxidative degradation of the pyrite and marcasite present in the refuse. Acid formation is partially attenuated b calcite or other neutralizing species in the refuse, but the leachates from th Illinois Basin refuse samples that we studied nearly always had pH values in t range of 2 to 4. These acid leachates are very efficient at dissolving or degrading many of the mineral components of the refuse, and thus releasing the trace or minor elements associated with them.

Two types of trace element leachabilities were observed for all of the Illinoi Basin refuse samples. Because of their abundances in the refuse some elements (such as Fe, Al, Ca, Mg) are released in relatively high absolute quantities. Other, less abundant elements (for example, Ni, Co, Zn, Cu) are leached in a high proportion to the total of each present, although this may not be a large amount in the absolute sense. The first group is highly concentrated in the leachates, the second is highly leachable from the refuse.

venting negative effects in exp
achievable through current technology. The utility of the MEG sys
provides a means for directly determining which of the contaminant
water solutions, such as those of interest here, exceed concentrat
safely assimilated by the environment. Application of the MEG rou
on the composition of refuse leachates obtained in this work, and
information in the literature, has revealed that nine elements, Fe
Ni, Zn, As and Cd are frequently present in potentially hazardous
though these elements are not necessarily the only ones in the ref
that could conceivably be troublesome under all circumstances, the
the priority elements that are receiving the greatest emphasis in
work on environmental control technology.

Two basic approaches to effect trace element controls are being co
this work. The first involves methods to treat newly produced coa
either at the preparation plant or during disposal to prevent the
lease of trace elements from the disposal site. These techniques
fuse calcining, treatment of the refuse to remove acid forming con
labile trace elements, and the application of adsorbents or attenu
to refuse disposal sites. The second approach concerns techniques
abate the trace-element composition of already contaminated waters
from refuse dumps or disposal areas. Under consideration here are
as alkaline neutralization, ion exchange, reverse osmosis, chelati
cation of selected adsorbents.

One of the more promising techniques under consideration to imobi
hazardous elements in high sulfur coal refuse materials is calcini
fuse to high temperatures to produce an inert glass-like slag. Pr
this area is directed both at identifying the chemical and physica
brought about in the refuse structure as a result of the heat trea
defining the consequent decreases in trace element mobilities.

An initial set of calcining experiments was performed using high s
preparation wastes from Plant B (Illinois Basin). The sample was
crushing the refuse to -3/8 in. and calcining it in a quartz tube
850°C in air for 6 h. The calcined material, which had partially a
was reground to -20 mesh for subsequent studies. The analysis of
composition of the calcined refuse sample showed that most of the e
retained in the calcined sample (Table I). A decrease in the conce
just a few volatile components in the refuse was noted. Of partic
was the loss of sulfur that occurred as a result of the calcining.
original concentration of 13.4% S by weight in the non-calcined sam
described sample treatment yielded a product that contained only 1
weight. From the standpoint of removal of the acid-forming constit
coal refuse, these results are quite remarkable since they show tha
in air at 800-850°C is a method that can substantially reduce the a
potential in the coal refuse wastes. Other volatile components who
trations were decreased by the calcining were Br, Pb, and Cd.

TABLE I

THE EFFECT OF CALCINING AT 800°C ON THE
TRACE ELEMENT COMPOSITION OF AN ILLINOIS BASIN
COAL REFUSE SAMPLE

Element[a]	Uncalcined Refuse	Calcined Refuse
Al (%)	5.9	11.5
Mn	144	191
Fe (%)	11.0	19.0
Co	30	70
Ni	71	110
Cu	35	73
Zn	149	296
Cd (ppb)	400	290
Pb	34	12
S (%)	13.4	1.1

[a]Elemental compositions reported as ppm unless otherwise indicated.

Another set of calcining and leaching experiments was performed to determine optimum heat treatment conditions necessary to chemically immobilize the poten- tially toxic trace elements in the refuse matrix. These experiments were per- formed using high sulfur coal preparation wastes from Plants B and C (Illinois Basin). The wastes were ground to -20 mesh and calcined in air at 600°C, 800° 1000°C, and 1200°C for 2 h. The calcined residues were then statically leache (stirred with distilled H_2O) for a period of 48 h using a ratio of 4 mℓ H_2O to 1 g of calcined refuse, and pHs and total dissolved solids determined. These data are summarized in Table II. It is seen that heating to 600°C and higher results in a leachate with an elevated pH -- this is a consequence of the re- moval of the volatile, acid-forming sulfur component and is consistent with th experimental data on sulfur volatilization. Calcining at 1000°C also results in a strong decrease in the leachate's total dissolved solids. Physically, th samples calcined at 1000°C showed signs of sintering. It appears, based on x- ray diffraction measurements, that at this temperature the clays have become glasses -- this results in a significant encapsulation and immobilization of

Sample Source	Calcining Temp., °C	Sample Wt. Loss, %	Leachate pH
Plant C	Uncalcined		2.9
Plant C	600	23	6.6
Plant C	800	23	6.2
Plant C	1000	23	7.8
Plant C	1200	23	8
Plant B	Uncalcined		1.8[b]
Plant B	1000	38	7.0

[a]Static leaching of 20 g of crushed refuse with 100 m⁴ of water for

[b]Leachate pH measured after 4.4 h of leaching.

illustrated by the data from a comparison leaching experiment involving
of the refuse samples (Plant C) that had been calcined at 1000 C (?
The calcined and uncalcined refuse samples listed in the table had
jected to static leaching for 48 h. It is seen from the information
table that calcining has essentially eliminated the acid generating
of the refuse samples and that the TDS contents of the resulting le
substantially reduced. More important is the fact that the concens
the abbreviated group of toxic elements listed have been reduced in
cined refuse leachates by about two orders of magnitude over the co
in the leachates produced from the raw refuse materials.

Several methods are being considered to treat coal refuse during d
prevent the release of trace contaminants during subsequent waste d
ing or leaching by surface or ground water. These include codispo
refuse material with neutralizing agents or trace element adsorbent
application of water tight sealants to all or parts of the waste du

Especially promising among these techniques is the codisposal of th
materials with alkaline agents such as lime. In one set of experim
example, powdered lime in varying amounts (3 to 50 g) was slurried
of distilled water with -3/8 in. high-sulfur coal refuse (530 g, fr
Basin Plant B). The resultant mixture was dried in air at 50 C, an

TRACE ELEMENT LEACHABILITY OF A PLANT C COAL REFUSE
SAMPLE CANCINED AT 1000°C FOR 2 H.[a]

	Uncalcined Refuse	Calcin Refus
pH[b]	2.9	7.8
TDS (%)	.6	.1
Al	100	<.5
Fe	600	<.03
Mn	5.8	.03
Co	2.8	<.01
Ni	4.7	<.01
Zn	2.8	.06

[a]Results from static leaching of 50 g of crushed refuse material
with 200 mℓ of water for 48 h.

[b]Leachate compositions reported as ppm unless otherwise noted.

to -3/8 in. particles. Four different lime concentrations were employed: 0.5
1.5, 3 and 10 wt %. In addition, a control refuse sample that had not been
lime-treated was also incorporated into this study for comparison purposes.

Column leaching experiments were conducted with about 500 g of each of the ab
samples to determine the effects of the lime additions. The refuse mixtures
were packed into pyrex columns 25 cm long by 5 cm diameter and subsequently
leached with distilled water at a flow rate of 0.5 mℓ/min until more than 4 ℓ
of water had been passed through the refuse beds. The compositions of the lea
ates after about 300 mℓ of water had passed through the columns containing the
refuse are given in Table IV.

Although the data are not listed in Table IV, the leaching experiments showed
that the addition of 0.5 and 1.5 wt % lime to the acid refuse had only a small
influence on leachate pH and trace element concentration because the acid
neutralization provided by these amounts of lime was overwhelmed by the acid
generating capability of the refuse. The additions of 3 and 10 wt % of the li
on the other hand (Table IV), did indeed effectively counteract the acid prop-
erties of the refuse; the pH of the leachates for these two systems are ele-
vated to acceptable levels and the trace element compositions of the leachates

	Untreated Refuse Control	Refuse + 3% Lime	Refus
pH[b]	2	7	
TDS (%)	4	0.4	
Al	720	<0.6	
Fe	7800	40	
Mn	22	1	
Co	12	0.3	
Ni	18	0.5	
Zn	29	0.1	

[a]Results from column leaching experiments with Illinois Basin Plan
(see text).

[b]Leachate compositions are reported as ppm unless otherwise noted.

The system containing 3 wt % lime is especially interesting becaus
of 7 was maintained for nearly the entire duration of the leaching
(until 4.2 ℓ had been passed through the column). TDS values for
lime combination were also very respectable (ranging downward from
wt %) especially considering that the dissolution of the lime itse
stantially to the dissolved solids content of the solution.

Another potentially fruitful way to retain the leachable contamina
refuse disposal site is to intermix the acid coal wastes with suit
of trace element attenuating agents. An example of one of the stu
in this area will illustrate the potential utility of the method.

In this experiment, acidic coal refuse leachates were equilibrated
solid sorbent materials to evaluate their trace element attenuatio
prior to using these agents in codisposal experiments. The solids
illite, montmorillonite, and kaolinite clays; a sample of scrubber
cipitator ash and two samples of bottom ash, each from different p
an acid drainage treatment sludge; and a clay rich soil. The exp
procedure consisted of shaking the solid (50 g) with

qualitative manner, the performance of the various sorbents with regard to leachate pH elevation, and attenuation of 13 trace elements that have been identified as being of greatest environmental concern in the Illinois Basin [] refuse effluents. The data have been isolated into different sections in Tal[] VI to draw attention to some of the pertinent features. For example, since t[] solubilities of Fe^{+3} and Al^{+3} are very sensitive to pH in acidic solutions th[] sorbents that are most effective in elevating the pH above a value of 5 are a[] most effective in decreasing the concentrations of Fe and Al. In Table VI wh[] the pH, Fe, and Al results are grouped together it is seen that 7 of the 11 [] sorbents tested are very effective.

TABLE V

THE ATTENUATION OF TRACE ELEMENTS IN COAL REFUSE LEACHATES BY VARIOUS ATTENUATING AGENTS[a]

	Untreated Leachate Control	Scrubber Sludge	Fly Ash	Ill[]
pH[b]	2.6	7.3	9.6	8.[]
Al	10	<0.2	0.6	0.[]
Fe	107	<0.1	0.2	0.[]
Mn	4	2.2	0.04	0.[]
Co	1.9	0.7	0.1	0.[]
Ni	2.6	0.8	<0.05	0.[]
Zn	1.0	0.6	0.02	0.[]

[a]Results from interaction of 50 g of attenuating agent with 150 mℓ of contro[]
leachate for 15 h.

[b]Leachate compositions reported as ppm.

TABLE VI

COMPARISON OF CAPABILITIES OF ELEVEN SORBENTS TO (a) ELEVATE pH AND (b) ATTENUATE THIRTEEN PRIORITY TRACE ELEMENTS IN ILLINOIS BASIN COAL REFUSE LEACHATE

SORBENT	pH	Fe	Al	Ni	Mn	Zn	Co	Cr	Cu	F	Cd	Na	K	Ca
CaCO₃	EEE	EEE	EEE	GG	EEE	EEE	GG	P	FF	GG	GG	P	P	P
CaCO₃ AMD Treatment Sludge	EEE	EEE	EEE	EEE	GG	GG	GG	GG	GG	GG	P	P	P	o
Illite	EEE	EEE	GG	GG	GG	FF	GG	GG	GG	P	GG	P	o	o
Precipitator Ash	EEE	EEE	GG	GG	EEE	GG	GG	o	FF	P	GG	P	P	o
Montmorillonite	EEE	EEE	FF	GG	GG	GG	GG	GG	FF	GG	FF	o	P	FF
Bottom Ash	EEE	EEE	EEE	FF	P	GG	FF	GG	P	P	FF	P	P	o
SO₂ Scrubber Sludge	EEE	EEE	EEE	FF	P	P	P	FF	FF	o	o	P	o	o
Alabama Soil	FF	GG	P	P	o	P	P	GG	P	P	P	P	P	P
Bottom Slag	FF	F	P	P	P	P	P	GG	P	P	o	P	P	P
Kaolinite	FF	GG	P	P	o	o	P	F	o	P	o	P	P	P
Sea Sand	P	P	P	P	P	P	P	P	o	P	P	P	P	P

EEE = >100x Reduction
GG = 10 to 100x Reduction
FF = 3 to 10x Reduction

drainage water that is contaminated with acids and toxic trace elements. Included among these are alkaline neutralization, ion exchange, reverse osmosis, chelation and biological treatment.

One of the most promising of these control techniques, alkaline neutralization, is currently used extensively to treat acid drainage from coal mines. While it is well known that alkaline neutralization is very effective in controlling the acid and overall salt compositions of mine waste waters, the degree of control that this method exerts over some of the more highly leachable toxic trace elements remains to be established.[1] Elaboration of this latter point is the basis for one of the studies now being conducted in this area.

TABLE VII

ALKALINE NEUTRALIZATION OF CONTAMINATED
COAL REFUSE DRAINAGE[a]

	Untreated Leachate Control	Lye	Limestone	Lime
pH[b]	1.1	6	7.1	6.6
TDS (%)	0.5	3.4	3.2	3.2
Al	18	<0.2	<0.2	<0.2
Fe	820	0.06	0.3	0.3
Mn	3.6	0.07	6.4	1.0
Co	2.0	0.05	1.0	0.6
Ni	3.2	0.05	1.0	0.7
Zn	3.9	0.02	0.1	0.1

[a]Results from addition of alkaline agent to 1ℓ of control leachate until indicated pH was achieved.

[b]Leachate compositions reported as ppm unless otherwise indicated.

a predetermined value of the pH was reached. The solutions (...) were allowed to sit overnight, filtered, and the pH, dissolved solids an(d) trace element contents of them were measured. The results of these expe(ri-) ments are summarized in Table VII.

Examination of Table VII shows that neutralization is an effective techn(ique) for decreasing trace element concentrations in refuse waste water. The (Al) and Fe contents of the treated solutions are within acceptable limits ba(sed on) the 1977 EPA effluent limitation guidelines for coal preparation plants (Fe ≤3.5 µg/mℓ averaged for 30 days, pH 6-9). Mn, however exceeds the a(ccept-) able level of 2.5-3 µg/mℓ (averaged for 30 days) in the limestone case; however, this was shown to be due to traces of Mn in the limestone used (in the) neutralization experiments. Further work in the area of alkaline neutra(lization) of refuse drainage involves its application to more highly contaminated (drainages,) to investigate coprecipitation phenomenon, and the scale up of the proces(s to) more life-like circumstances.

SUMMARY

The purpose of this paper has been to present an overview of research un(derway) at the Los Alamos Scientific Laboratory to investigate experimentally so(me of) the more attractive options for controlling trace element contamination (of) refuse drainages. The control methods under consideration include chemi(cal) and physical methods to immobilize or remove undesirable contaminants pr(ior to) refuse disposal, the treatment of refuse disposal sites with attenuating (agents) or sealants to prevent the discharge of contaminated water, and the dire(ct) treatment of refuse drainage as it emerges from the refuse disposal site(s. The) initial quantitative results from these laboratory studies suggest that t(he) techniques being considered are technically feasible for effectively cont(rolling) trace element contamination of refuse dump drainage.

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IMPLICATIONS OF ANALYSIS OF HIGH GRADIENT
MAGNETIC SEPARATION TO COAL RELATED APPLICATIONS

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Abstract

The cross section for particle collisions with an
isolated magnetized fiber in air and water is given as a
function of the physical parameters of the filter system.
Two models for using the cross section to predict real
filter efficiency are discussed. The analysis of particles
in air shows a strong dependence of cross section on parti-
cle inertia and gravity and pronounced maxima in the cross
section at small particle radii, features which are not
present in liquids. The cross section in air is especially
sensitive to particle size at small particle radii and to
the free stream velocity. The cross section in air is
reasonably large for a range of conditions, which supports
the view that economically practical applications of mag-
netic filters in air-particle separations may be possible.

A number of other practical applications were pointed
Oberteuffer[5] and recently many specific filtration p
in air and liquid streams, including coal related appl
have been discussed.[6]

The basic physical idea underlying the operation
gradient type devices is simple: If a ferromagnetic fi
placed in a magnetic field it becomes magnetized and a
particles. Many thin fibers placed transversely to th
netic field form a fibrous filter which, although suff
porous to allow a relatively free flow of fluid, captu
carries a substantial load of magnetic impurities.

Work carried out at METC has been concerned with t
standing of the basic physical elements of the filtrat
process. These studies have been on the dynamics of t
ture of particles by an isolated fiber and by a fiber
interior of a regular lattice of fibers. Here we summ
the results and discuss their application to the analy
the performance of real filters. We consider two diff
models for calculating the filter efficiency, the isol
model and regular lattice model.

The cross section for capture has been calculated
isolated fiber and for a fiber in the interior of a la
fibers.[7] These calculations show that for a highly
filter, say fiber spacings greater than eight fiber ra
cross section for the isolated fiber and a fiber in a
are approximately equal. This does not mean that ther
interference effects in porous filters, for even thoug
cross sections may be nearly equal in the two cases, t
of the shadows (in particle density) cast by fibers ca
affect the efficiency of the filter as a whole. The i
fiber model neglects entirely the interference, includ
shadows, of neighboring fibers, whereas the lattice mo
siders the fibers as a coherent array and accounts for
effect of the lattice as a whole on particle trajector
isolated fiber model gives an optimistic estimate of t
ciency of a real filter whereas the lattice model shou
vide a low estimate. We discuss first the isolated fi
and present functional dependence of the clean fiber c
section on the filter parameters. The regular lattice
discussed in section 3.

2. Isolated Fiber Model

In a filter with fiber perpendicular to the strea
the capture distance, x_c, is the maximum value of the
impact parameter for which the particle trajectory int
sects the fiber and the cross section for capture per

particle density, Δn, is $2x_c n \Delta y/\alpha^2$ and it follows that the
efficiency of a filter of depth y is $1 - \exp(-2x_c y/\alpha^2)$.
These hypotheses explicitly neglect the shadows, i.e.,
neglect the nonuniformities in particle density in the
transverse direction caused by capture of particles from
the stream. For particles greater than 1 μm we do not
expect that diffusion of particles into the shadows is
sufficiently rapid to maintain the assumed transverse uni-
formity.

In the isolated fiber model the cross section is
calculated in the approximation which neglects the effects
of neighboring fibers. The interference effects are accou
for by introducing an empirical factor, say k, in the expo
nent of the efficiency formula. If the fibers are oriente
in random directions with respect to the magnetic field,
only that fraction of the fibers perpendicular to the fiel
should be counted, which correction may also be absorbed
in the empirical factor k. If the theory is used to
represent a filter operating over a period of time, the
corrections to the cross section for buildup of particles
on the fibers given by Luborsky and Drummond [8] and
Watson [9] should be applied.

Even though the empirical correction required to brin
calculated and observed efficiencies into agreement is qui
large, [8,10,11,12] the isolated fiber model has been usefu
for identifying the significant physical parameters and
for giving roughly correct functional dependence of effi-
ciency on the parameters.

The isolated fiber cross section has been calculated
by Watson [13] and Luborsky [4] for inertialess particles
and by Lawson et al. [14] for particles with inertia.
Usually, particle inertia is negligible for filtration of
liquids and significant for filtration of gases, at least
for the size range usually considered in magnetic separati
A well known order of magnitude argument shows that the
onset of inertial effects should be expected at stokes
number, K, greater than 0.1. However, even though the
shapes of particle trajectories are in fact affected by
inertia [14,15] at $K > 0.1$, the net effect of inertia on
capture cross section is small up to $K = 1$ for cross secti
greater than a fiber diameter.

An idea of the range of particle size and free stream
velocity for which particle inertia is negligible may be
obtained from figure 1. To the left of the $K = 1$ curves
particle inertia is negligible in the computation of cross
sections for cross sections greater than a fiber diameter
for a fiber diameter of 200 μm.
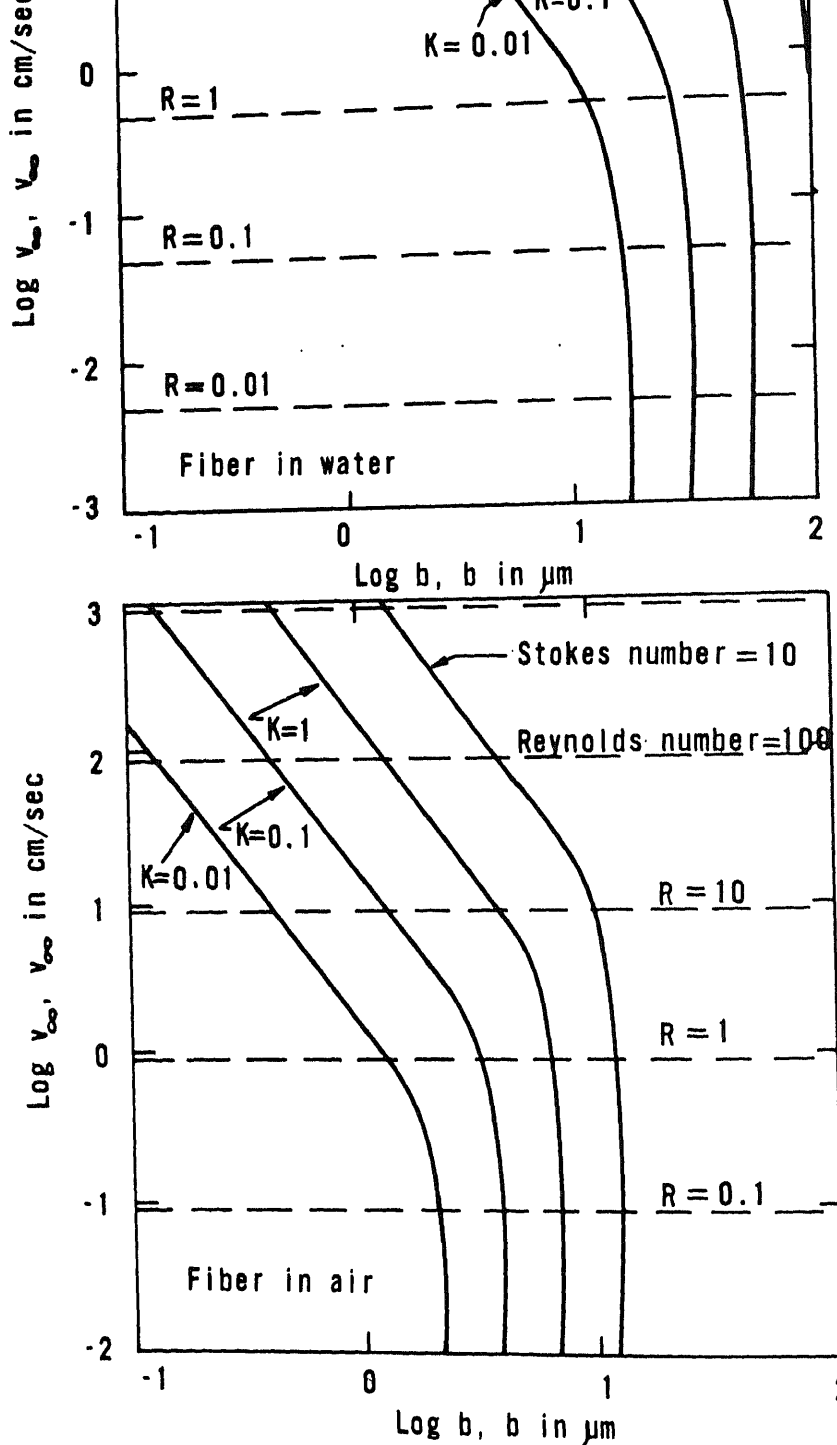
Figure 1.- Curves of constant Stokes number and constant number for a 200 μm diameter fiber in water and air.

fluid field, but for cross sections greater than a fiber di
meter the error incurred by this approximation may not be
excessive.

The isolated fiber cross section has been calculated
a broad range of conditions which include filtration in ai
For conditions such that particle inertia and the gravita-
tional force are negligible, the cross section depends on
single dimensionless parameter.[13] This parameter is the
ratio of a magnetic quantity, v_m, with the dimensions of
velocity and the free stream velocity v_∞. Increasing v_m/v
either by increasing v_m or decreasing v_∞, increases the cr
section.

When particle inertia and the gravitational forces ar
significant, the cross section is a function of three dime
sionless parameters,[14,15] v_∞/v_T, the Stokes number and
v_m/v_T, where v_T is the terminal velocity of a particle fal
parallel to the free stream. The expressions for the sign
ficant parameters are

$$v_T = v_\infty + \frac{2\rho_p b^2 g(\rho_p - \rho_f)}{9\eta} ,$$

$$v_m = \frac{2\chi B b^2 M}{9(1+\chi/3)\eta a} ,$$

$$K = \frac{2b^2 \rho_p v_T}{9\eta a} .$$

There are nine physical quantities involved here, the part
properties,

ρ_p, mass density,

b, radius,

χ, magnetic susceptibility,

the fluid characteristics,

ρ_f, mass density,

η, viscosity,

M, magnetization density of the fiber, and

B, the external magnetic field strength.

The dependence of cross section on the dimensionle[ss]
parameters v_m/v_T, K and v_∞/v_T is shown in figures 2 and
There have been observations of trajectories and cross s[ec]
tions for particles in air[15] which are in agreement w[ith]
cross sections shown here, which provides a check on th[e]
theory for a small range of the parameters considered.

The cross section is shown in figures 4 to 11 as a [function]
of the physical parameters B, b and v_∞. The cross sect[ions]
are for particles in air and water for low, moderate an[d]
particle susceptibility. As discussed above, in the is[olated]
fiber model, the cross section is used to calculate the [effi-]
ciency from the expression

$$\text{efficiency} = 1 - \exp-\left(\frac{k2X_c ay}{\alpha^2}\right),$$

where $X_c = x_c/a$ is the cross section in units of the fi[ber]
diameter. Taking $k = 1$ neglects fiber orientation and [inter-]
ference effects entirely and provides an upper bound on [the]
efficiency of a real filter. In section 4 we will disc[uss]
certain prominent features of the cross section curves [but]
first we consider the lattice model of a filter.

3. Regular lattice of Fibers.

We give now a brief description of the regular lat[tice]
and the results of the calculation of trajectories and [cross]
section. The details of the analysis and full account [of]
results are given in reference 7. The lattice consists [of]
parallel circular fibers with fiber axes perpendicular [to the]
magnetic field. The fluid flow and gravitational field[s are]
parallel and directed oppositely to the magnetic field. [Both]
rectangular and rhombic lattices have been studied.

The external magnetic field magnetizes the fibers [and]
each fiber acquires a uniform magnetic moment per unit [of]
length in the direction of the magnetic field. The res[ulting]
field is the external field plus the field caused by th[e mag-]
netized fibers. The fluid field is the sum of the unpe[rturbed]
flow and the fluid disturbances caused by the circular [fibers.]
We have developed analytical expressions for the result[ing]
fields which represent a lattice with its longest dimen[sion]
in the direction of the field. From these expressions [the]
forces on a magnetic particle in the interior of a latt[ice]
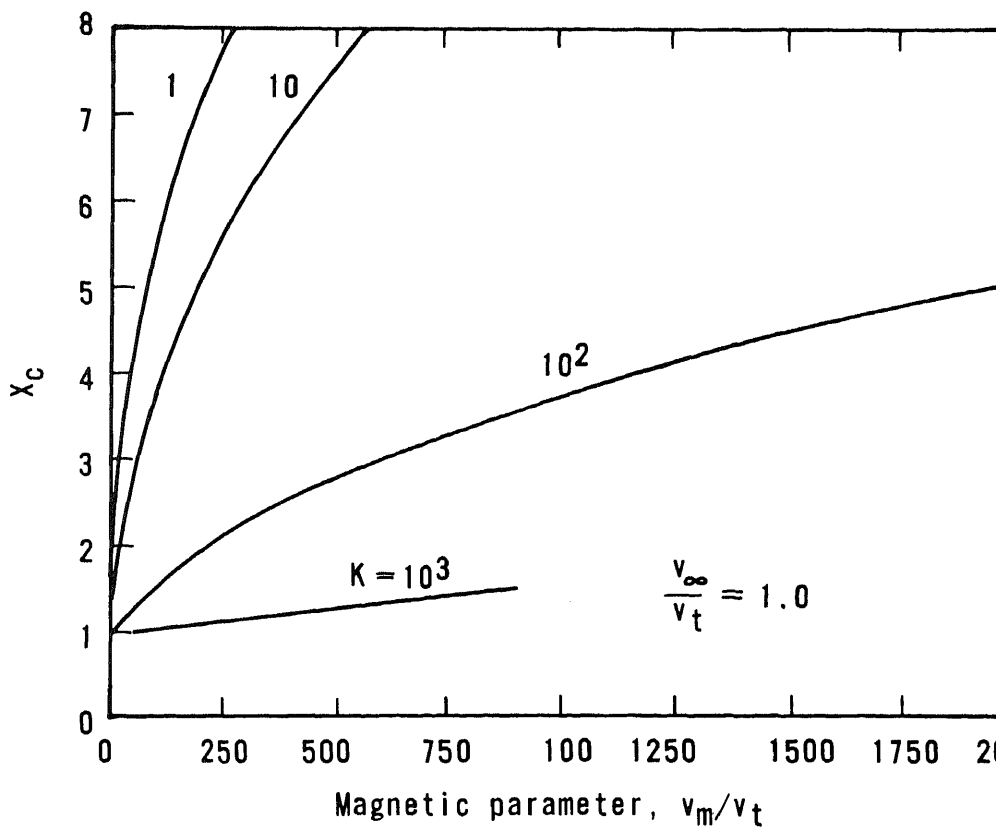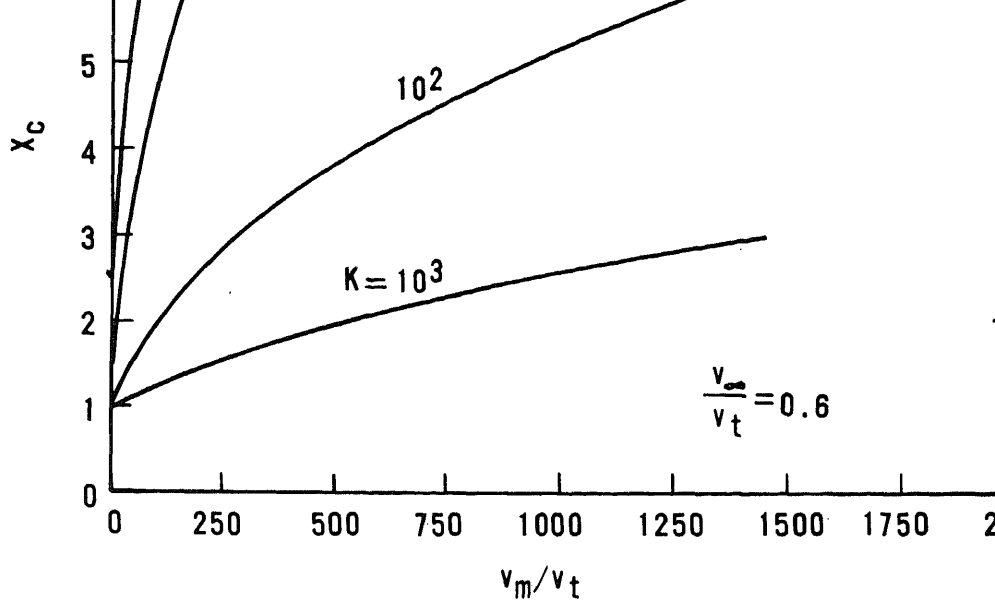
Figure 2.- Cross section as a function of v_m/v_t for fixed Stokes number, K, and gravitational parameter v_∞/v_t.
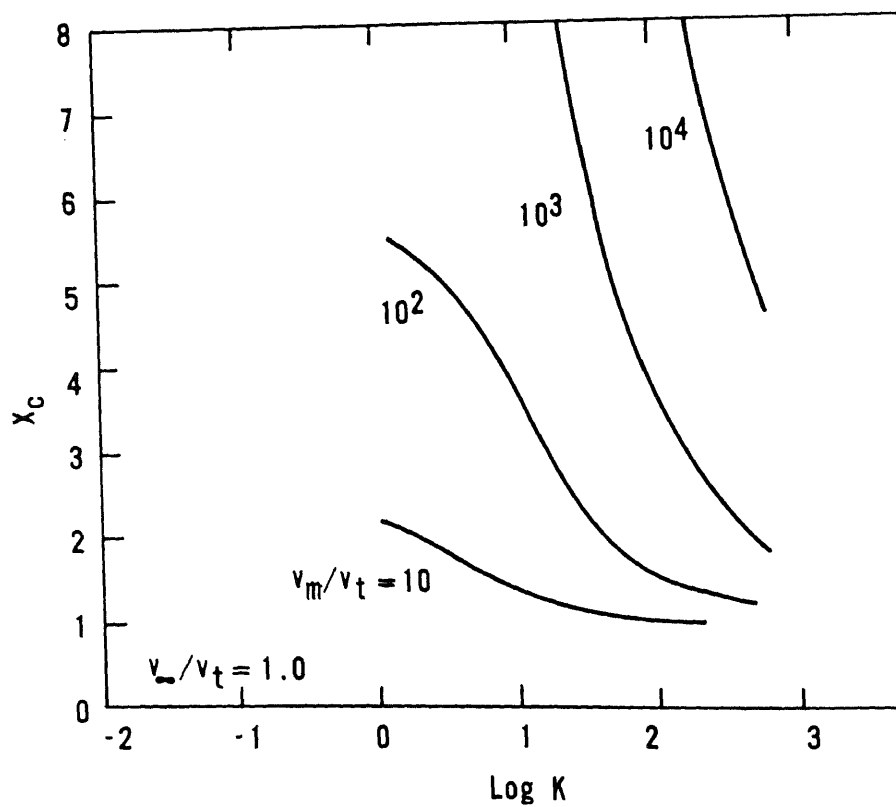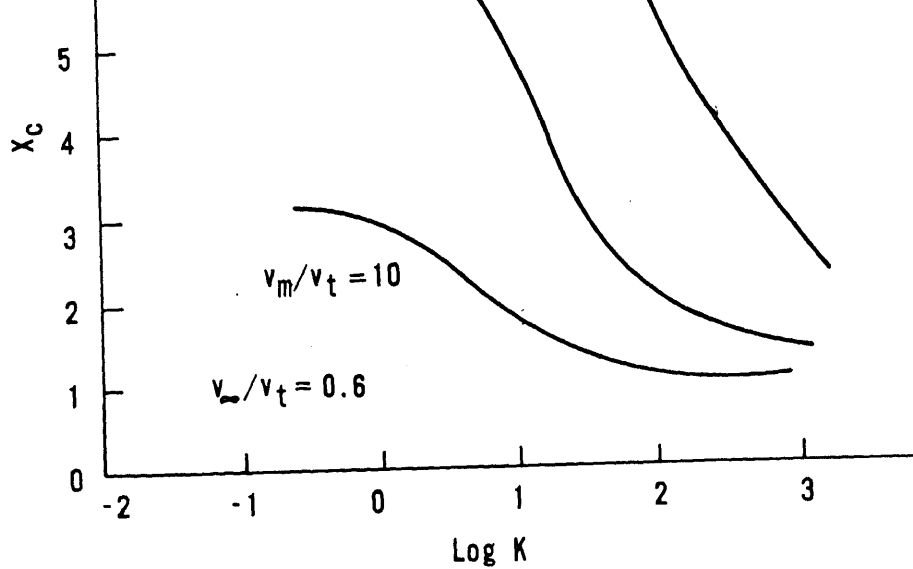
Figure 3. - Cross section as a function of Stokes num
for fixed magnetic parameter and gravitational parame
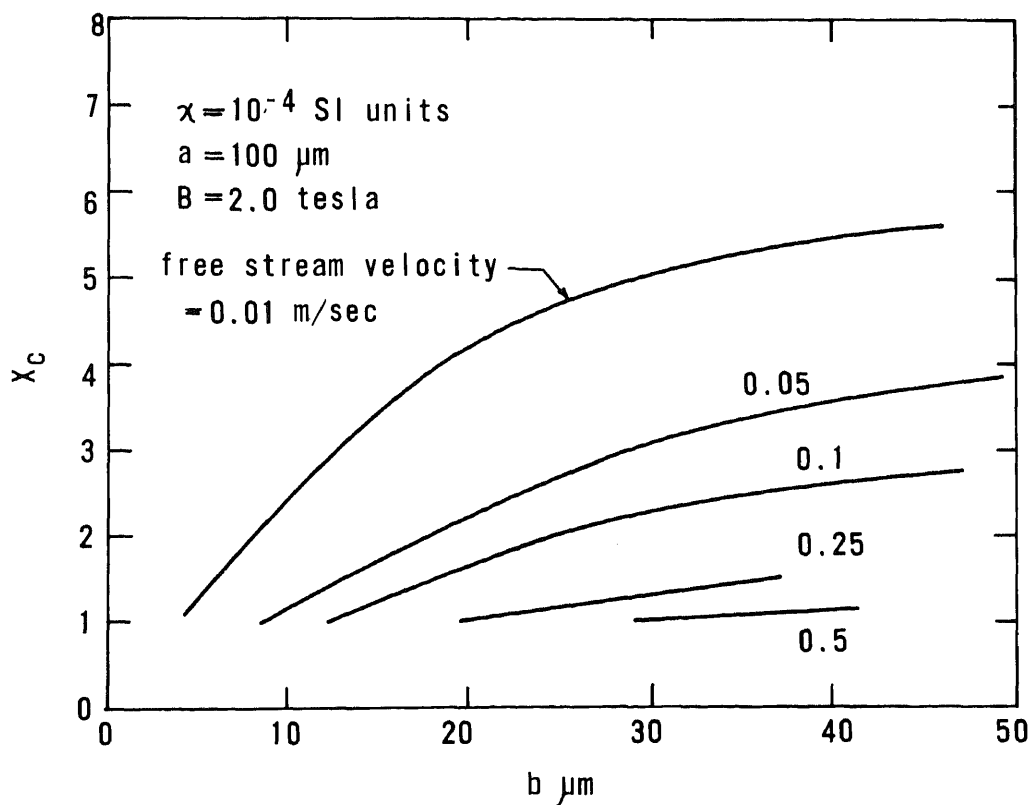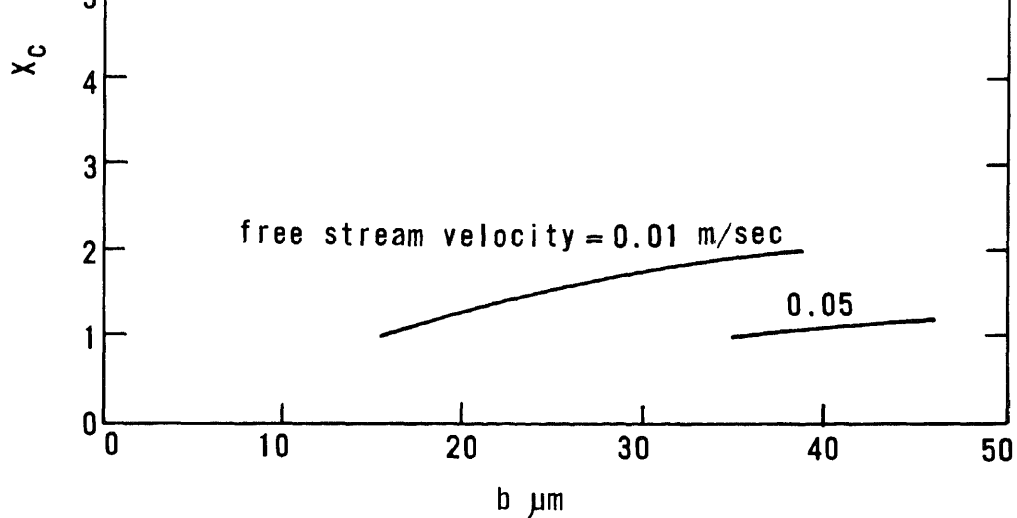
Figure 4.- Cross section in water as a function of particle rad
parametrized by the free stream velocity, v_∞, for fixed low
particle susceptibility and two values of the magnetic field.
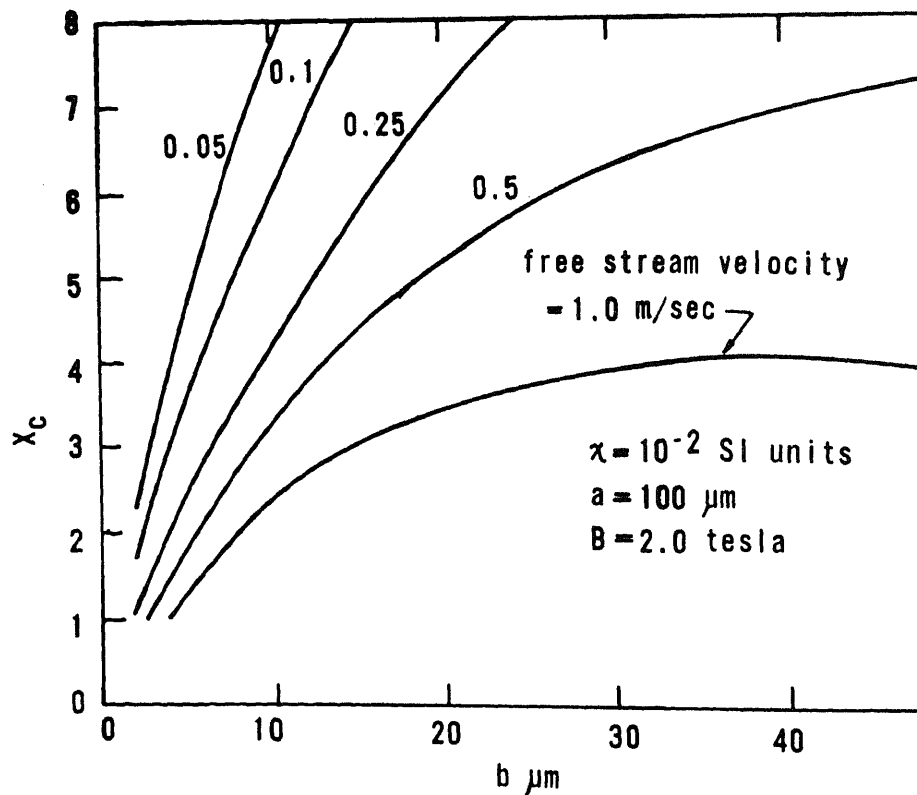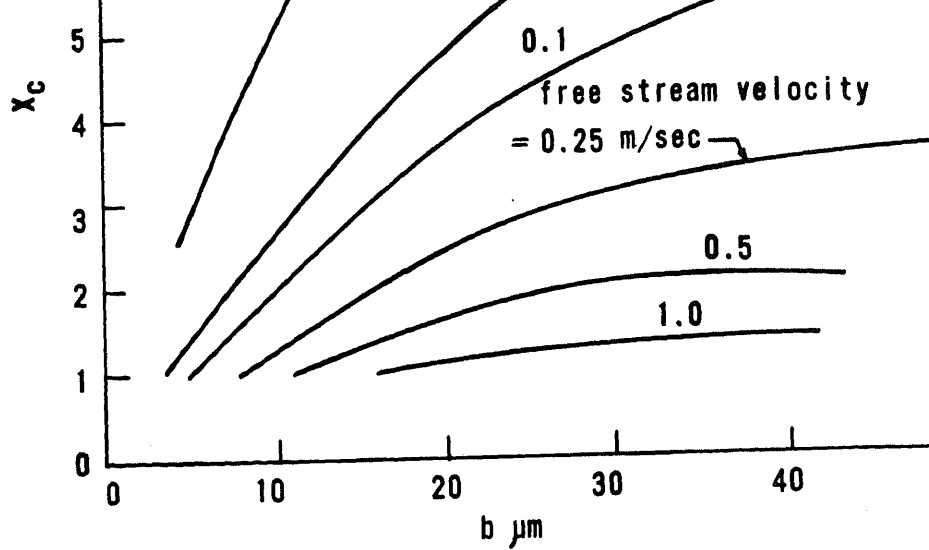
Figure 5.- Cross section in water as a function of partic[le]
parametrized by the free stream velocity, v_∞, for fixed [h]
particle susceptibility, χ and two values of the magnetic
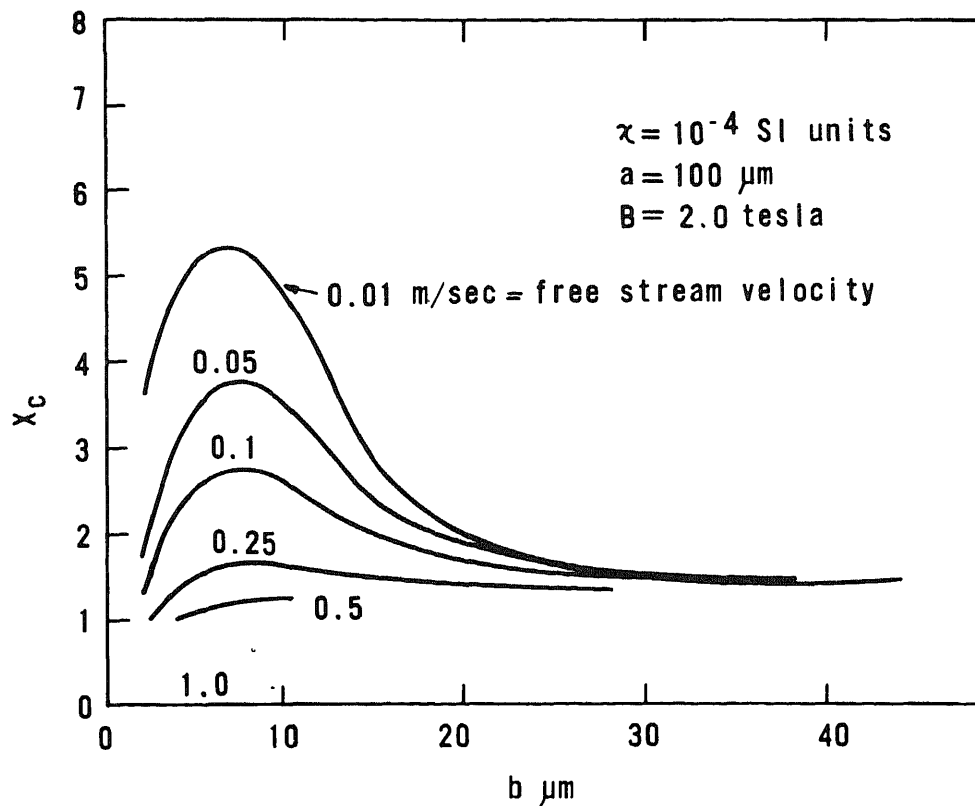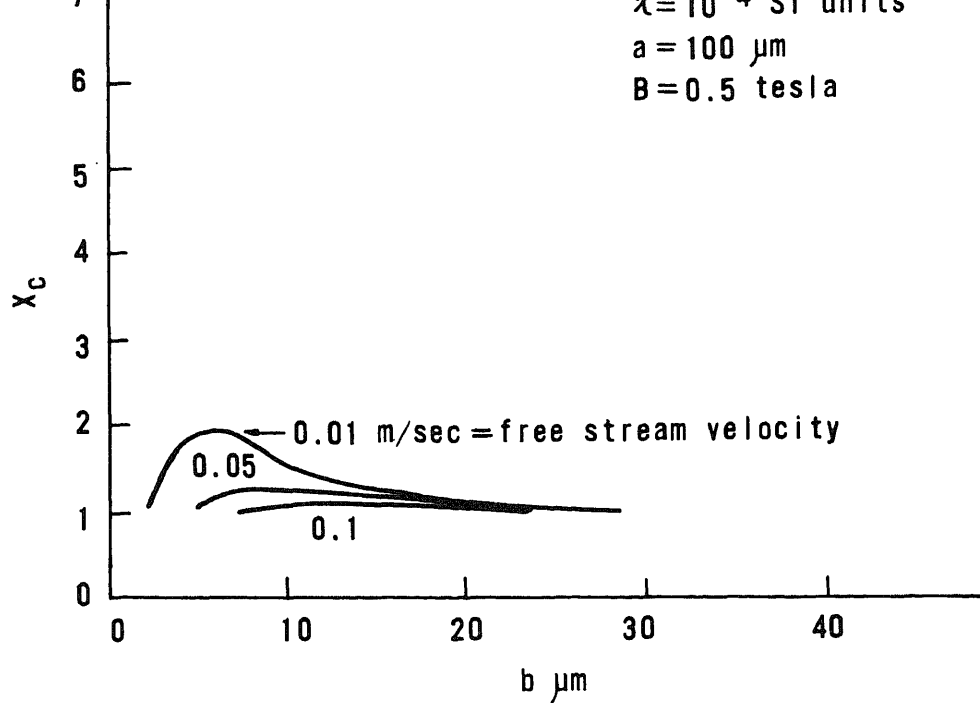
Figure 6. - Cross section in air as a function of particle radius, parametrized by the free stream velocity, v_∞, f[or] fixed low particle susceptibility and two values of the
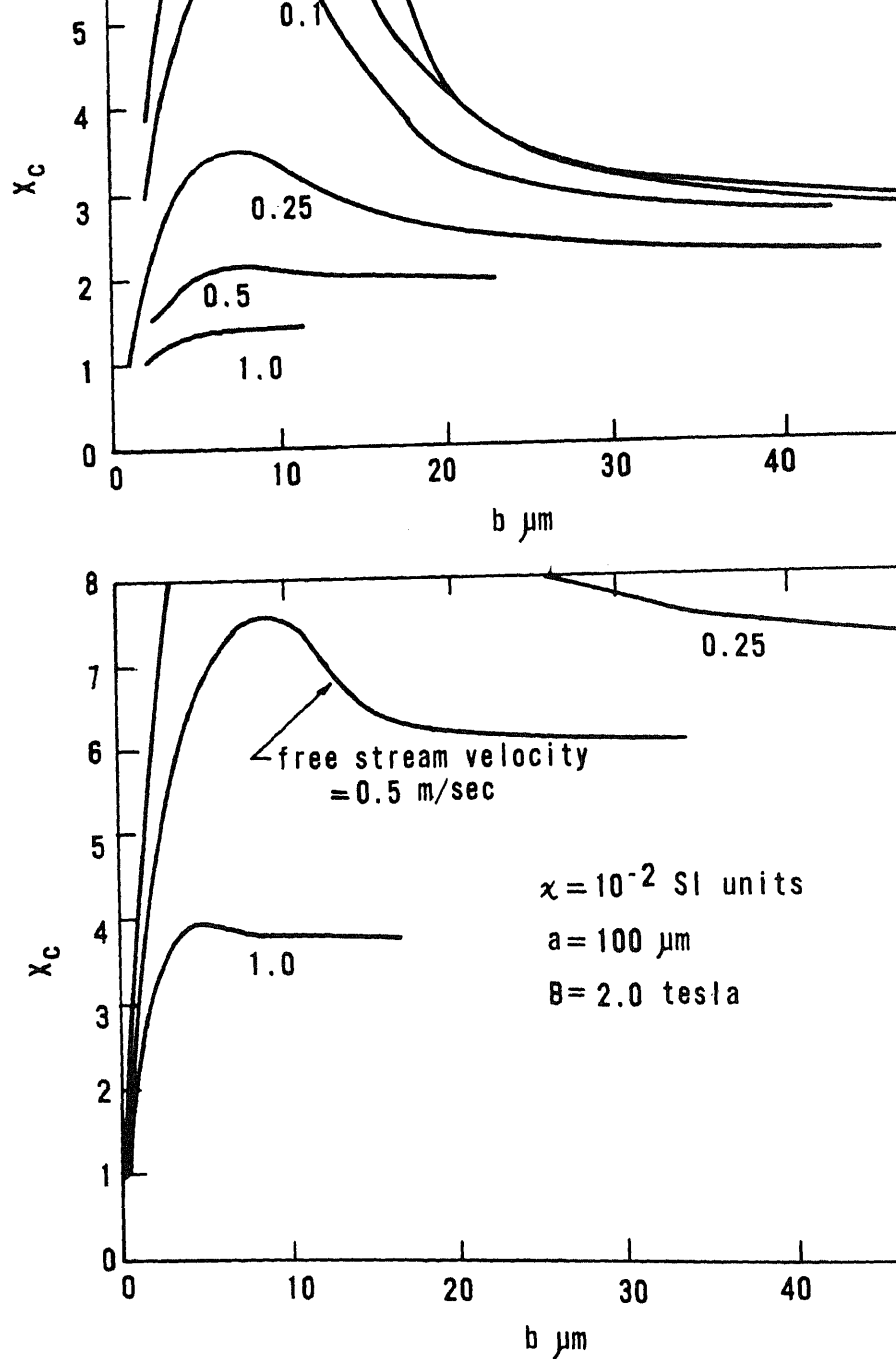
Figure 7. - Cross section in air as a function of pa[rticle]
radius, parametrized by free stream velocity, v_∞, f[or]
high particle susceptibility χ and two values of mag[netic]
field B.
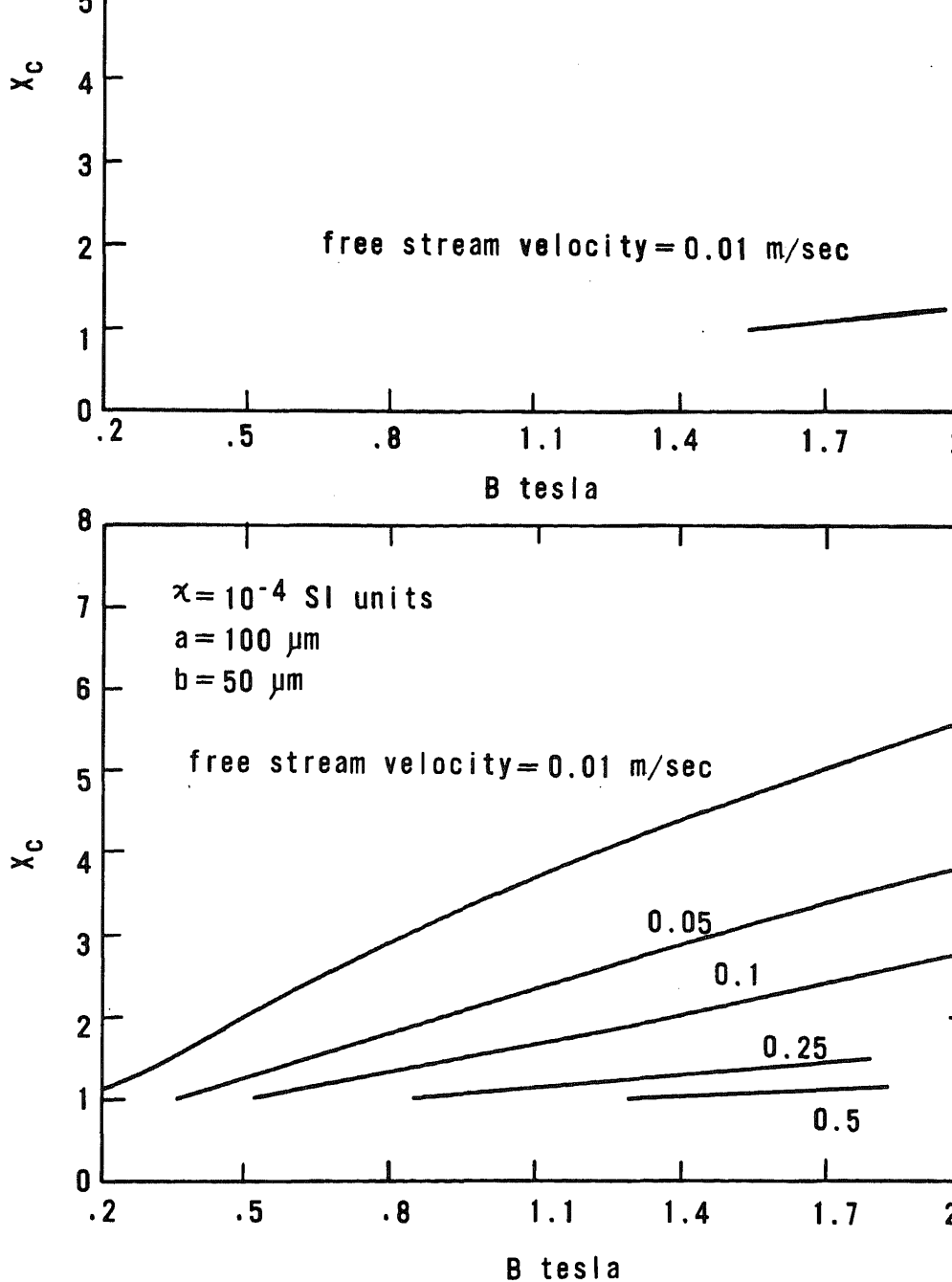
Figure 8.- Cross section in water as a function of magnet
field, parametrized by the free stream velocity, v_∞, for
low particle susceptibility and two particle radii.
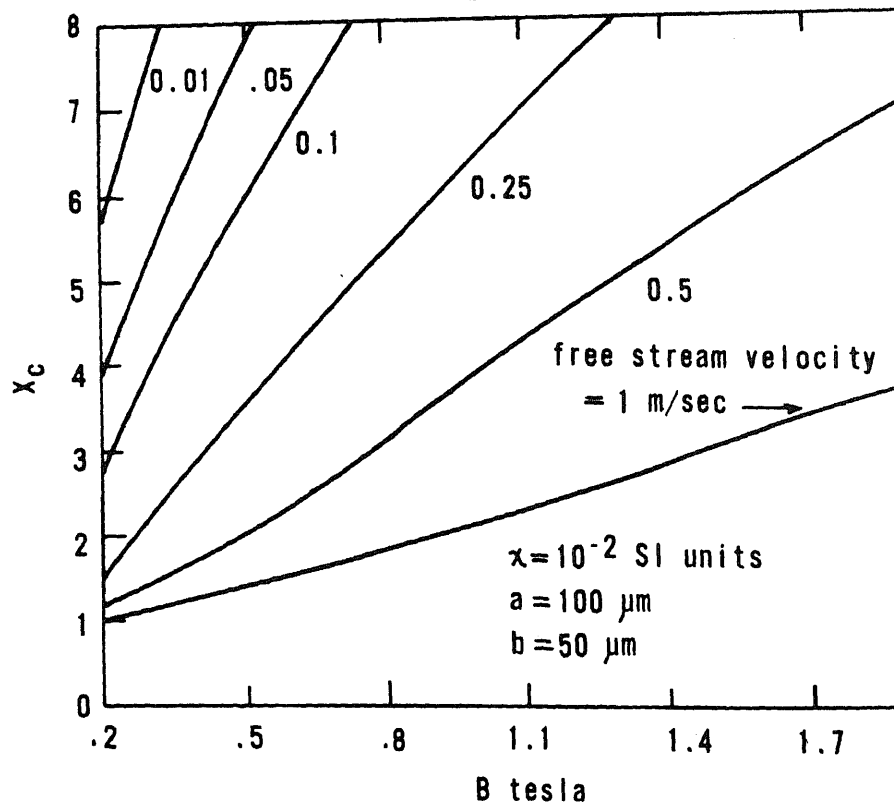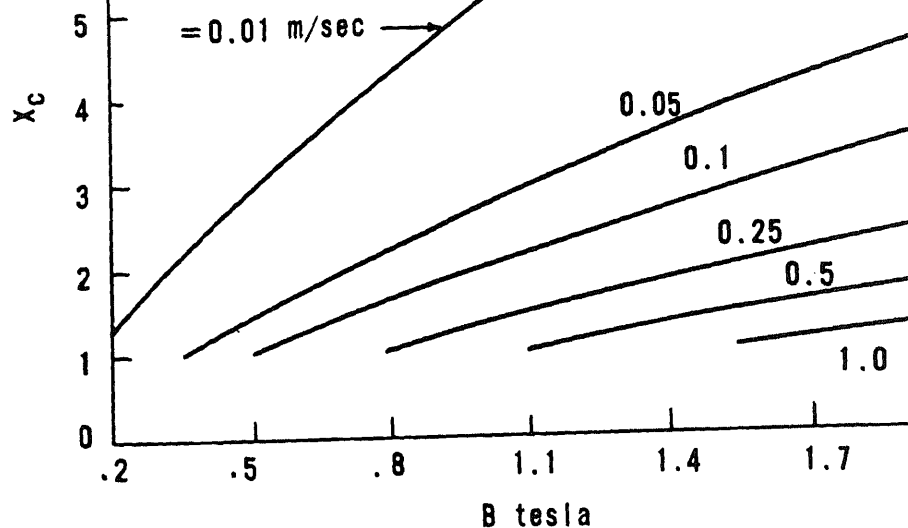
Figure 9.- Cross section in water as a function of mag[netic]
field, parametrized by the free stream velocity, v_∞, f[or]
fixed high particle susceptibility and two particle ra[dii.]
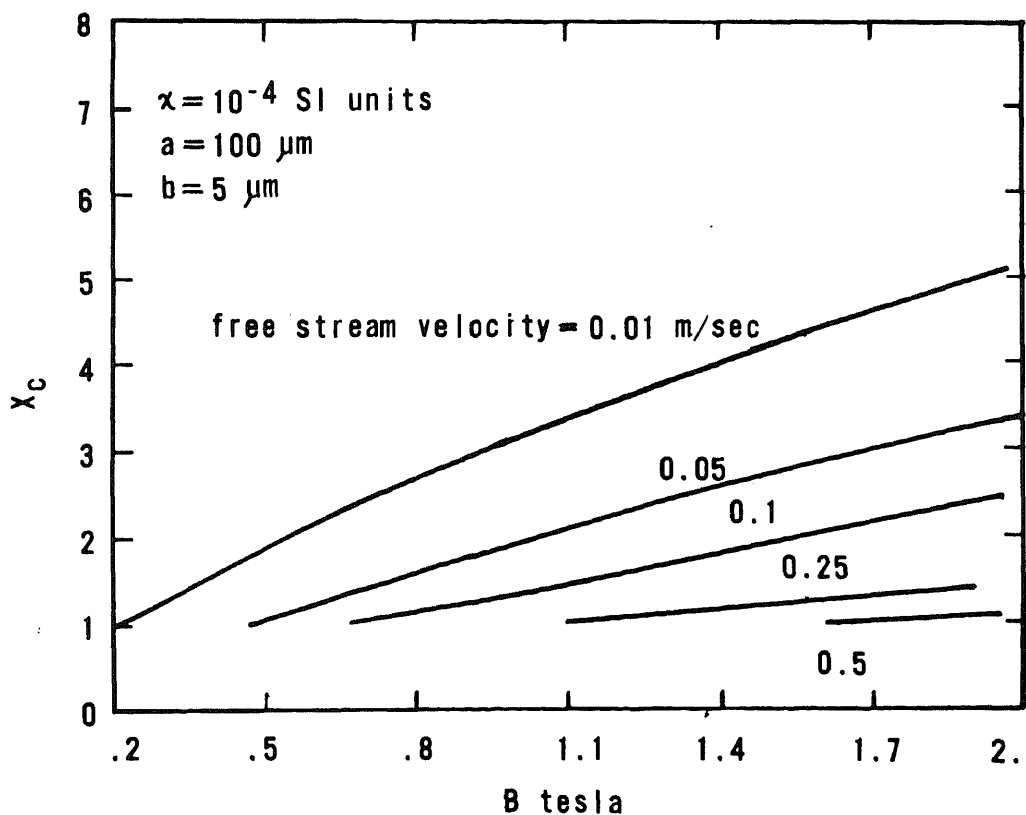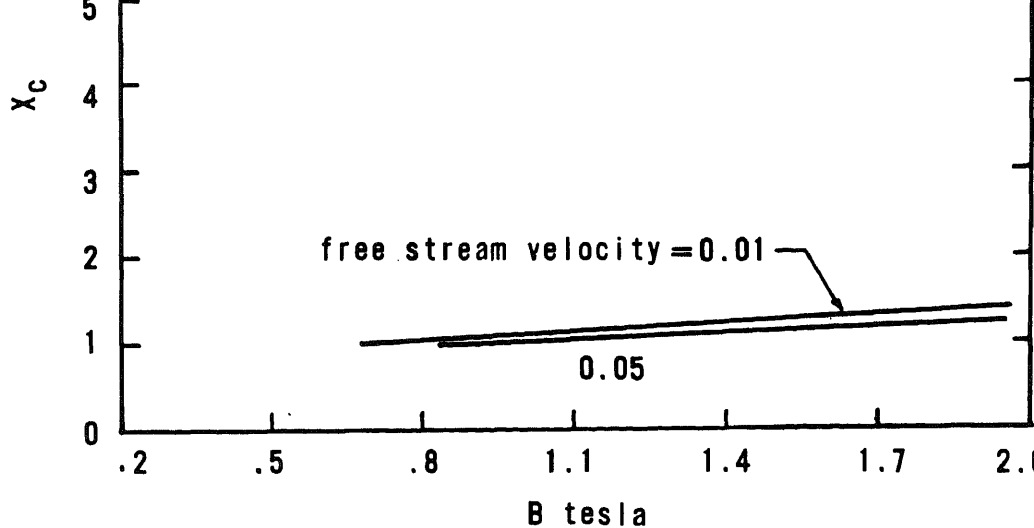
Figure 10.- Cross section in air as a function of magnetic field, parametrized by the free stream velocity, v_∞, for f low particle susceptibility and two particle radii.
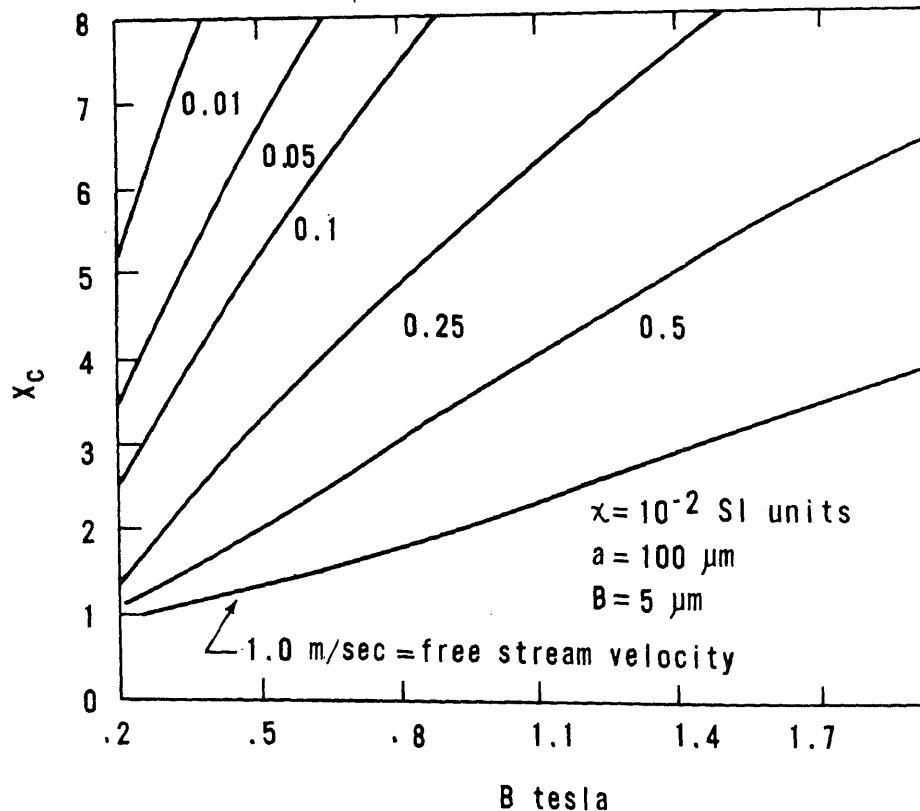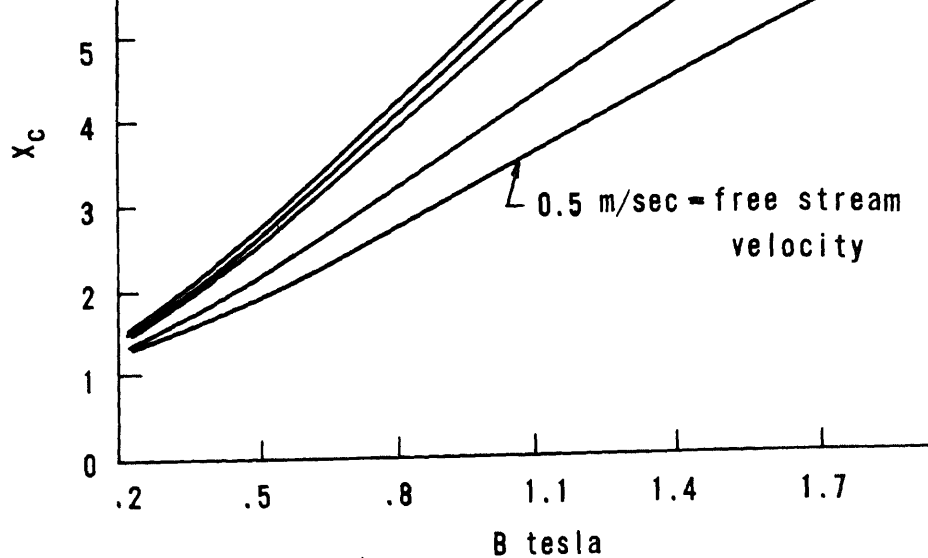
Figure 11.- Cross section in air as a function of magne
field, parametrized by the free stream velocity, v_∞, fo
high particle susceptibility and two particle radii.

forces, Newton's equation of motion for a particle is form
The equation has been integrated in the approximation whic
neglects particle inertia, and trajectories and cross sect
have been obtained. The cross section is shown in figure
as a function of v_m/v_T for a fixed horizontal distance bet
fibers and different spacings in the vertical direction fo
both rectangular and rhombic lattices. Multiplication of
cross section shown in figure 12 by $\alpha/2a$, where a is the f
radius, gives the cross section in units of fiber diameter
allows a comparison with the isolated fiber cross section.
For fiber separations $\alpha/a \geq 8$, the isolated fiber and the
in a lattice cross section are not greatly different.

Particle trajectories in the rhombic and rectangular
lattice are shown in figure 13. Because of the periodicit
of the force field the pattern of trajectories found in on
cell will be repeated throughout the lattice. It is seen
trajectories are separated into those which intersect the
fibers and those which do not. Trajectories which enter a
an upper cell boundary and do not get captured will leave
that cell and enter the cell below. Since this pattern is
repeated these trajectories will not intersect any of the
fibers below. Thus, excape channels are formed which perm
particles to pass through the filter. The width of the ch
depends on v_m/v_T and can be made as narrow as one pleases
increasing v_m/v_T, e.g. by increasing the magnetic field.

One sees at this point an essential difference betwee
the filter efficiencies of the isolated fiber and the latt
models. Assuming a horizontally uniform distribution of p
cles entering the lattice the number of particles passing
through the filter is proportional to the width of the esc
channel, which is $\alpha - 2x_c$ in the case of the rectangular l
tice. The filter efficiency is thus, simply, $2x_c/\alpha$. A si
result holds for the rhombic lattice. As noted above the
limit $2x_c/\alpha = 1$, which implies an impenetrable fiber layer
can be obtained for sufficiently large v_m/v_T. It is note-
worthy that the lattice efficiency is independent of filte
depth in contradistinction to the exponential dependence
obtained from the isolated fiber model.

We expect that the lattice model gives a low estimate
of real filter efficiency. The regularity and complete
coherence of fibers in the lattice probably includes the
effects of shadows rather too strongly, whereas, the isola
fiber viewpoint neglects completely the fiber shadows. A
better description would seem to lie somewhere between the
models.

4. Discussion

The dependence of the cross section on the parameters
the system is shown in figures 4 to 11. The cross sectio
used to compute the efficiency of a clean porous filter ac
ing to the discussions in sections 2 and 3.
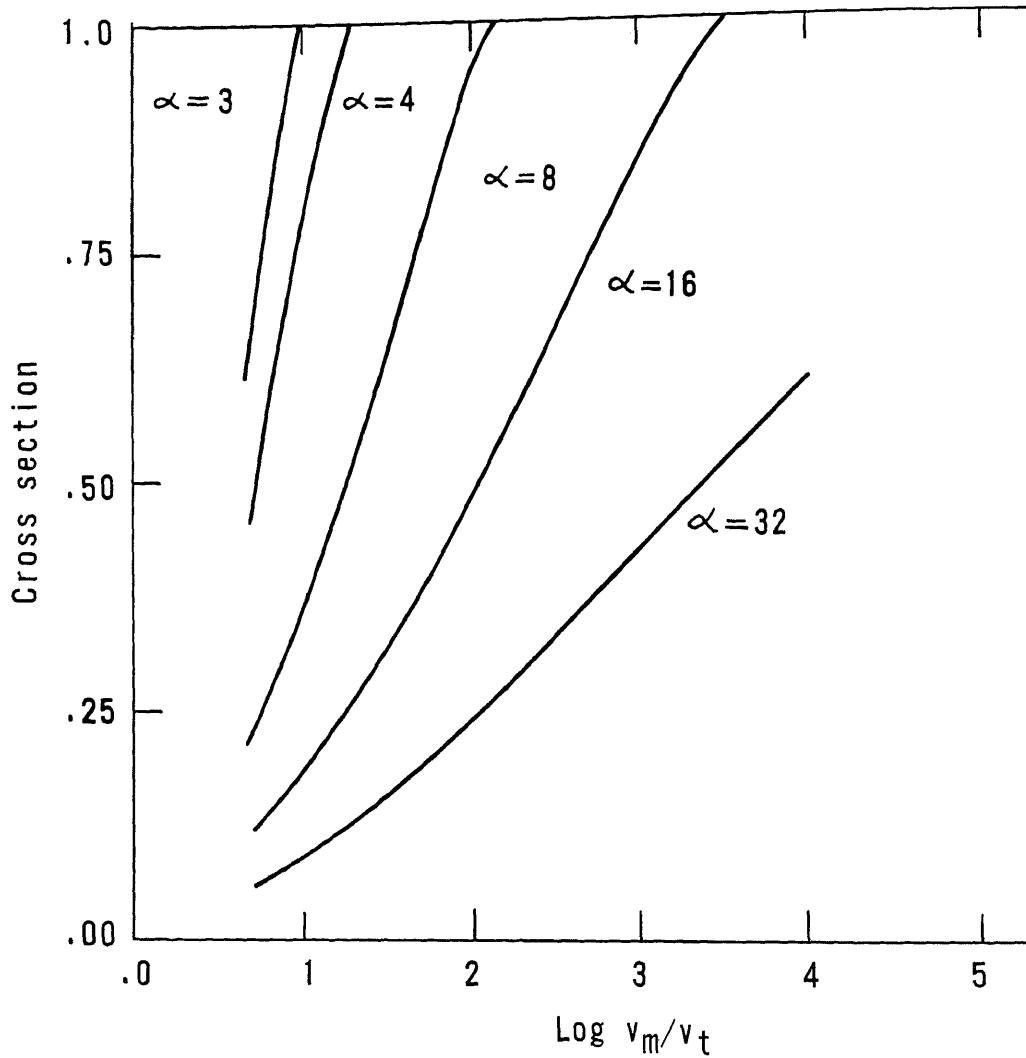
Figure 12.- Cross section for a fiber in rectangular lat
function of magnetic parameter with horizontal distance
fibers fixed at $\beta = 8$.
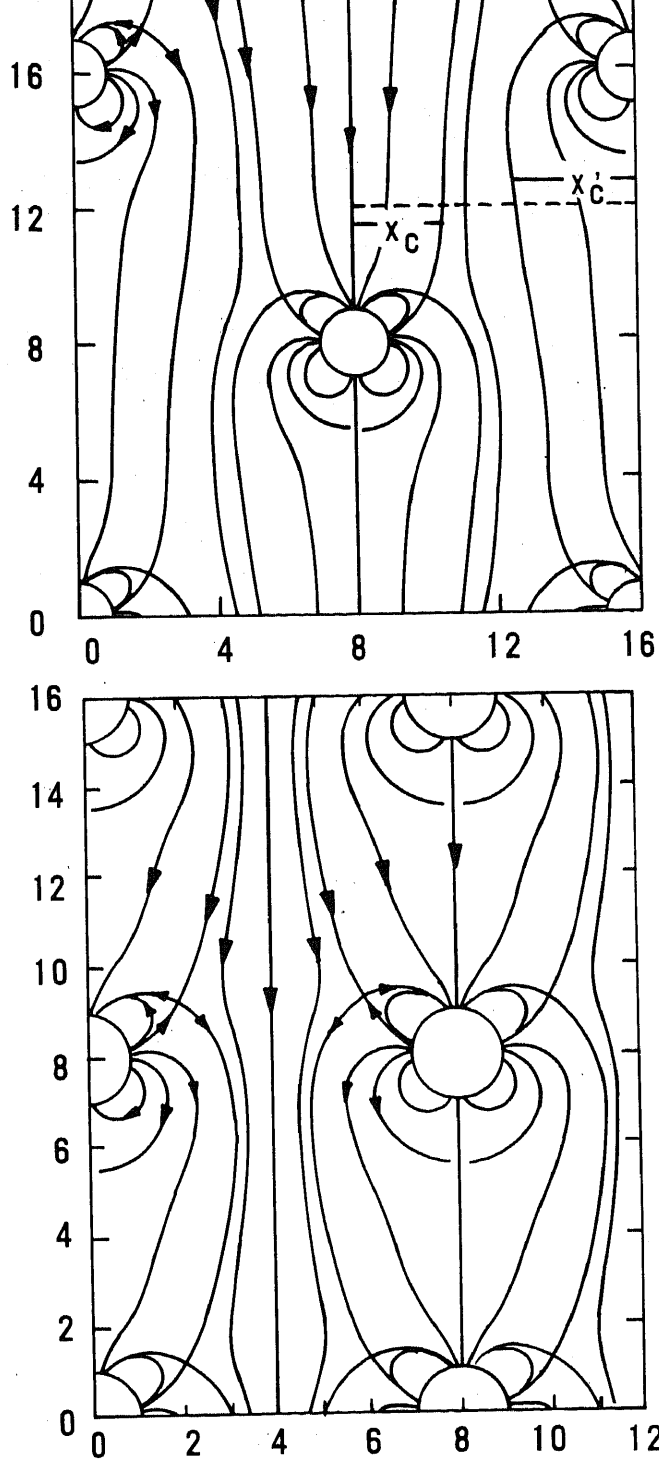
Figure 13. - Particle trajectories in 8x8 square and rhombic lattices showing escape channels.

nearly coincident with the K = 1 curve. This shows the absence of inertial effects for K < 1. Th
This shows the absence of inertial effects for K < 1. Th
magnitude of the parameter v_∞/v_T is a measure of the eff
of the gravitational force. For example, if $v_\infty/v_T = 1$ tł
is no gravitational effect and $v_\infty/v_T = 0$ corresponds to a
particle falling past a fiber in still fluid.

The cross section as a function of Stokes number, p
metrized by the magnetic parameter, is shown in figure 3
One sees the strong decrease of cross section with Stoke
number at large Stokes number. This behavior makes it d
cult to obtain large cross sections in air at high free
velocities. However, at moderate and low velocities it
not hard to obtain rather large cross sections. For exa
in air for a moderate particle susceptibility, $\chi = 10^{-3}$
units, magnetic field B = 1.0 tesla, particle radius 15
and iron fibers of radius a = 100 μm, we obtain from the
expression on page 4, $v_m = 18$ m/sec. Then if $v_\infty = 0.2$ m
we have $v_m/v_T = 54$, $v_\infty/v_T = 0.6$ and K = 47, the latter n
being in the inertial range. Referring to the upper gra
in figure 3 (or figure 2) we obtain a cross section of a
two fiber diameters.

Figures 2 and 3 and the numerical example illustrat
point which has already been appreciated, for example, b
Gooding et al.[11]: The flow velocity is an especially s
parameter in the magnetic filtration of air. It is of c
also important in liquids, but in air higher velocities
generally required and the cross section decreases with
creasing velocity by virtue of a decrease in the magneti
parameter and an increase in Stokes number. Whereas, in
inertialess condition, typically realized in liquids, th
Stokes number dependence is absent.

Figures 4 to 7 show, for air and water, the depende
cross section on the particle radius. It is often noted
high gradient magnetic separation is especially suited f
filtration of fine particles. Although this method may
better than others one nevertheless notes that in water
monotonic increase of cross section with particle size f
the capture of the larger particles.

In air, where inertia is important, both v_m/v_T and
increase with increasing b and the competing effects res
in pronounced maxima in the cross section shown in figur
6 and 7. Roughly speaking, the maxima are caused by the
increase in v_m/v_T with b at small b and the increase in
minal velocity and particle inertia having a dominant ef
at high b and bringing the cross section down.

The monotonic increase of cross section with the ma
field shown in figures 8 to 11 is simply due to the incr
in the magnetic parameter when the other parameters are

5.   Summary

The theoretical cross section for the collision of pa[r]ti-
cles with magnetized fibers is given as a function of the
physical parameters of the filter system. The cross secti[on]
for particles in liquid is well known and the graphs for
water given here show only additional details of the funct[ional]
dependence on the parameters. The relatively large cross
sections found in liquid have encouraged the investigation[s]
of practical applications. The results presented here fo[r]
particles in air extend existing results. The cross secti[ons]
are reasonably large for an interesting range of condition[s]
which supports the view that filtration of fine particles
in air may be economically practical.
Unfortunately it is not possible, at this time, to
predict with reasonable accuracy the efficiency of a real
filter with the aid of the isolated fiber cross section. [We]
suggest that the interference effects in real filters are
very important and are not accounted for correctly either [by]
the isolated fiber model or the lattice model. Neverthele[ss]
the isolated fiber cross section has been a reliable indic[ation]
of the qualitative behavior of real filters. In air the [indi]
cation is that the fiber cross section and hence the filte[r]
efficiency is very sensitive to free stream velocity, and [the]
cross sections will be relatively low for applications whi[ch]
require moderate magnetic fields and free stream velocitie[s of]
1 m/sec and larger. Of course filter efficiency can alwa[ys]
be increased by increasing the density of fibers and dept[h of]
the filter but only at the expense of pressure drop acros[s]
the filter. The analysis in air also shows maxima in the
cross section at about 10 μm which are not present in liqu[id.]
The maxima are very pronounced at low velocities and tend [to]
disappear as the free stream velocity is increased.

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INTRODUCTION

Coal production is expected to increase significantly over the n
20-year period with coal serving as the primary fuel for electrical gen
tion, replacing dwindling supplies of domestic oil and gas, and reducin
dependence on expensive imported oil and gas. Coal production will als
increase to meet the needs of the emerging gasification and liquefactio
industries. The increased tonnage will be from new mines or from expan
of existing mines; many of these mines will be (or are) located in coal
fields east of the 100th meridian. This line, lying east of the North
Dakota lignite field and west of the Texas coal fields, roughly divides
country into two regions: a western region of low-sulfur coal where rai
is usually less than 26 inches/year, and an eastern region where rainfa
generally exceeds 26 inches/year and most of the coal (lignite excepted
well as the rocks overlying the coal, often has a relatively high sulfu
content. Sulfur in the eastern region is primarily in the form of iron
pyrite. Mining eastern region coals exposes the pyrite to oxidation, r
in ferrous sulfates which produce acid upon hydrolysis. The acidic wat
or is pumped from the mine and, unless effectively treated, leads to se
environmental degradation of streams and lakes within the watershed and
potential health hazards from a polluted drinking water supply.

In early FY 76 a program was begun at Argonne National Laborator
(ANL) to evaluate technologies for controlling the environmental impact
effluents resulting from the surface mining of coal. The program is be
performed for the Department of Energy's Division of Environmental Cont
Technology (DOE-ECT) as part of ECT's overall mandate to assess the eff
ness of methods for controlling pollutant emissions from energy extract
conversion, and utilization processes. Initial support for this study
"pass-through" funding from the U.S. Environmental Protection Agency (E
current support comes from DOE-ECT.

This program has a twofold purpose which is related in part to t
interests of its two federal sponsors. The overall issue addressed by
sponsors is the need to satisfy increased coal demand in an environment
acceptable manner. Each sponsor, however, has particular objectives.
is interested in an evaluation of the efficacy and practicability of co
mine effluent control options currently in use, an identification of co
technology needs, and recommendations for research. The EPA is interes
in an assessment of the validity of the recently promulgated effluent g
lines for the coal mining industry, with this assessment emphasizing se
and climatic variation impacts on effluent quantity and quality. A pro
plan was outlined to: (1) project future coal production levels to the
2000 as a basis for selection of case study sites; (2) gather data at
surface mine case-study sites on effluent volumes and characteristics a

scneary. Phase I of the program examines eas...
Phase II will examine western mines.

The results of this program are providing data for federal and
industrial decision-makers concerned with: (1) developing criteria for
choosing the "best" environmental control option; (2) policy decisions
involved in the siting of future coal facilities; and (3) establishing a
basis for national judgments on the practicability of present and antici...
environmental standards.

The program interacts with the National Coal Association, 15 coal
companies, 12 universities, and 10 state and federal regulatory/research
agencies.

PROGRAM PLAN

This program is focused on the assessment of alternate control te...
nologies that show promise for environmentally safe handling of effluent...
and wastes from strip mining operations in the eastern region (east of th...
meridian) coal fields through the end of the century. The program has be...
divided into five tasks, and a unit operations master plan developed whic...
shows the interrelationship of the tasks (Fig. 1):

TASK 1 - FUTURE COAL PRODUCTION SCENARIOS
AND CASE STUDY SITE SELECTION

In this effort ANL estimated future coal production levels through...
year 2000 and identified areas east of the 100th meridian where surface m...
coal production is expected to increase. A series of maps was produced s...
each state's coal fields, active mines producing over 200,000 tons per ye...
and proposed new mine openings. A series of computer-drawn maps of each
state's coal reserves also was completed; these maps show total, surface,
and deep minable reserves for each county where data is available. From
maps and from contacts with the National Coal Association, industry sourc...
and the U.S. Bureau of Mines, twenty-one areas were chosen as the most li...
places for increased production. Mines were selected for each area which
typified local coal field conditions. Permission was obtained from mine
company officials to use the mines as case study sites from which data co...
be gathered regarding the volume and character of mine effluent discharge...

TASK 2 - MINE DRAINAGE GEOCHEMISTRY

An intensive sampling program was developed to determine the volum...
and characteristics of mine effluents at each of the twenty-one case stud...
mines. All mines were coded to shield their identity. Consultants under...
Argonne supervision conducted sampling activities; samples were obtained
the mine pit discharge point before any treatment and at the treatment di...
charge point, thus obtaining a measure of the treatment efficiency. Samp...
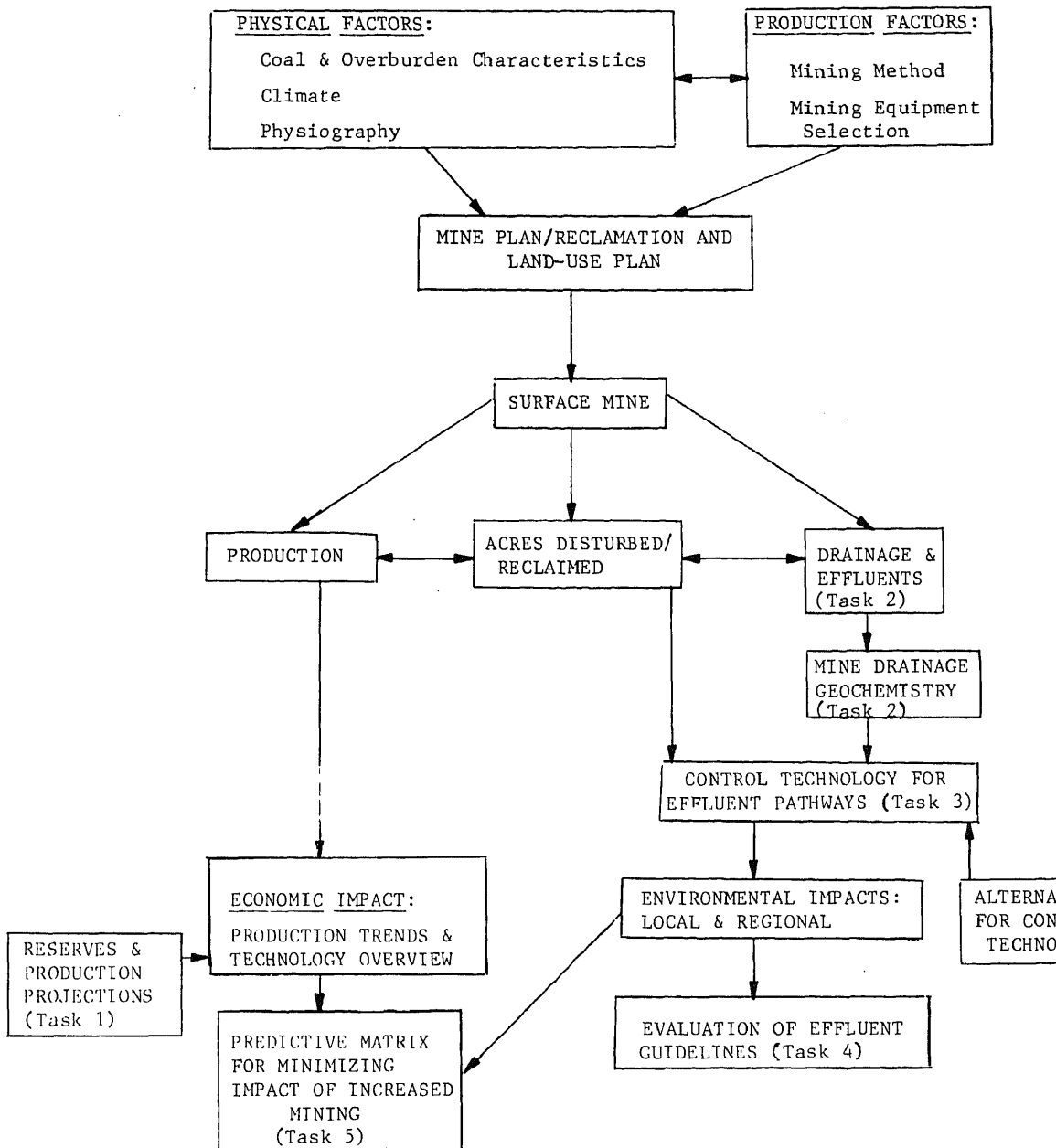
Fig. 1. Unit Operations Master Plan

Temperature	Manganese
Conductivity	Aluminum
pH	Sulfate
Dissolved oxygen	Chloride
Acidity/alkalinity	Fluoride
Total dissolved solids	Strontium
Total suspended solids	Magnesium
Iron	Ammonia
Sodium	Potassium

Trace element analysis was performed every three months. Elemen[ts]
analyzed included:

Mercury	Vanadium
Cadmium	Molybdenum
Cobalt	Nickel
Chromium	Lead
Copper	Zinc

The overburden was sampled and analyzed for major, minor, and t[race]
elements, and forms of sulfur. Coals were sampled and underwent proxi[mate]
and ultimate analyses in addition to the same types of analyses perfor[med]
on the overburden. Acid potential (derived from pyritic sulfur) and
neutralization potential were also determined.

The field sampling phase has been completed and the data are be[ing]
reviewed and analyzed. Argonne is analyzing the sample data and asses[sing]
the environmental impacts and pollution potential for each site. This [assess]
ment, coupled with the information relative to the increased coal prod[uction]
and control technology options, will provide the baseline data for a r[eport]
on the potential environmental impacts related to increased surface mi[ning]
through the end of the century. Figure 2 summarizes the various opera[tions]
for Task 2.

TASK 3 - CONTROL TECHNOLOGY ASSESSMENT

Mine effluent quality is being examined before and after treatm[ent]
to provide a measure of the effectiveness of the treatment process. C[ontrol]
technology cost data are being obtained whenever possible. Process wa[ste]
products are being identified and characterized, and the economics of [their]
disposal/reclamation are being considered. The environmental impacts [of the]
waste products generated by the various treatment process and selected
alternative processes are being studied. Figure 3 indicates the ideal[ized]
unit operations for control technology assessment at surface coal mine[s.]

A data management system for computer storage of the data gener[ated]
under this program has been selected and implemented. All relevant av[ailable]
storage and retrieval systems were reviewed, and System 2000 was selec[ted]

SAMPLING & ANALYSIS

COAL & OVERBURDEN CHARACTERI

CLIMATE: TEMPERATURES &
PRECIPITATION

MINE METHOD
EQUIPMENT

SAMPLING
& ANALYSIS

CHARACTERISTICS & VOLUMES OF
SURFACE WATER & GROUNDWATER
ENTERING MINE

MINE DRAINAGE

SAMPLING & ANALYSIS

MINE DRAINAGE
GEOCHEMISTRY

COMPARISON OF MINE
DRAINAGE GEOCHEMISTRY
TO GEOCHEMISTRY OF STREAM
BASIN WATERS

ENVIRONMENTAL
IMPACT

Fig. 2. Subunit Operations: Mine Drainage Geochemistry (Task 2)

DIRECT PRECIPITATION → SURFACE MINE
SURFACE WATER →
GROUNDWATER →

WATER COLLECTION

SURGE & EQUALIZATION

HOLDING POND

NEUTRALIZATION   REAGENT(S) → REACTION CHAMBER/
                                   MIXER

AERATION   AERATION POND/
                                  SLUICE/CHAMBER

FLOCCULATION   FLOCCULANT(S) → SETTLING
                                   POND(S)

                    H₂O   SLUDGE
                    OUT   DISPOSAL

(NO CHEMICAL TREATMENT)

POSSIBLE   ENVIRONMENTAL
ALTERNATIVE   IMPACT
TREATMENT(S)
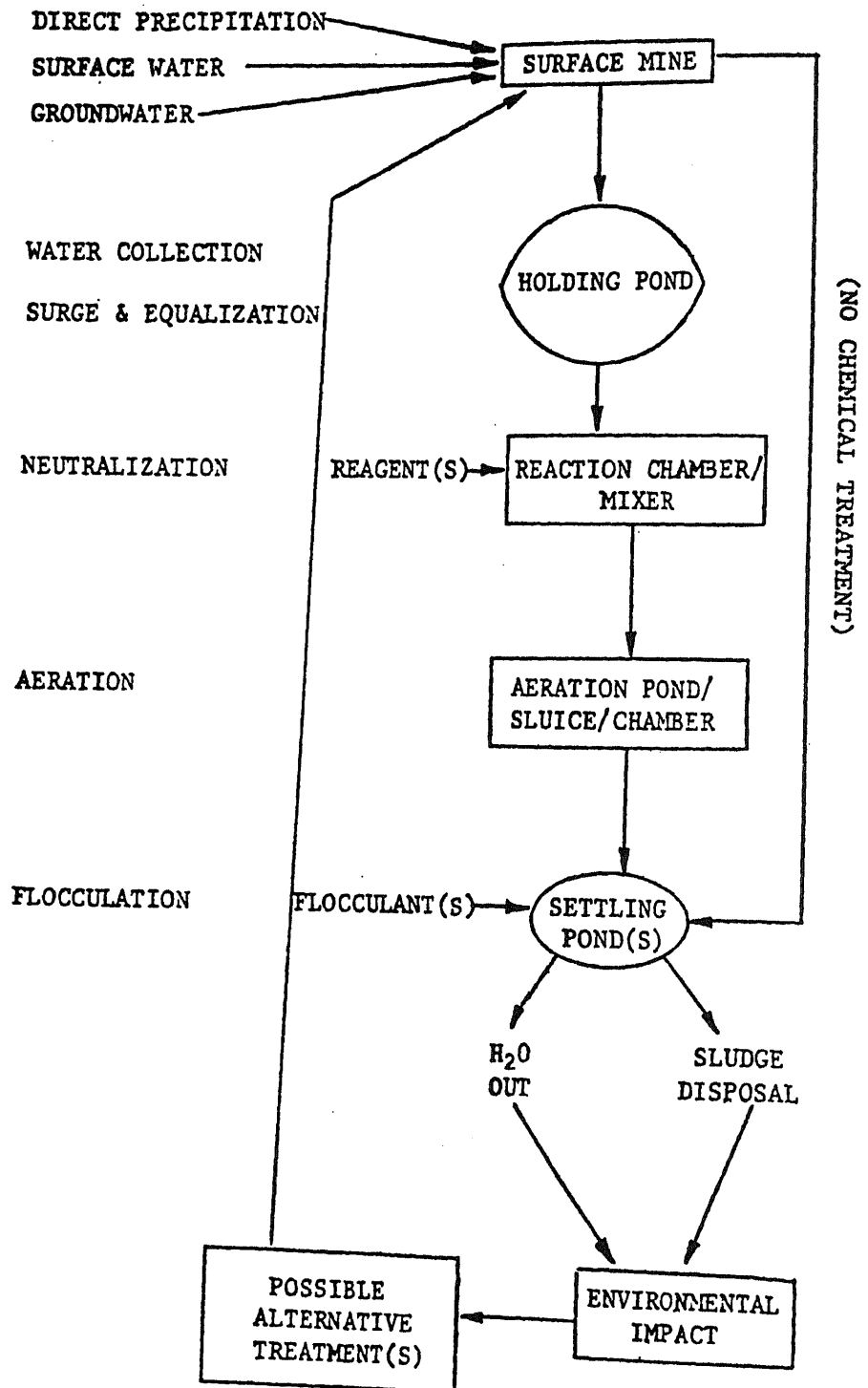
other data bank storage and retrieval systems. Input data include chemic
analyses of surface water, coal, and overburden, as well as background
information on sites and methods of sampling and analysis.

TASK 4 - EFFLUENT LIMITATIONS GUIDELINES

The mine effluent analytical data gathered under Task 2 are being
examined in relation to EPA's recently established effluent limitations
guidelines and new source performance standards for the coal mining point
source category. These standards and effluent limitations have been inco
porated into the Office of Surface Mining Reclamation and Enforcement's
proposed rules for a permanent regulatory program. The applicability of
guidelines and standards on a national scale versus state or regional sca
will be analyzed. The data from this program will be used to assess the
validity of the guidelines in general and in relation to current and futu
technology. Recommendations for modifying or implementing the guidelines
will be developed. Figure 4 shows the operations which will be utilized
in Task 4.

TASK 5 - SUMMARY REPORT

Argonne National Laboratory will write a summary report integrati
chemical data from the various sites with a discussion of generic environ
mental control problems, the pollution control technology involved, and
the control technology effectiveness. Included in this final report will
be recommendations for environmentally effective control technology for a
of new mine openings, and alternate control technologies for existing and
expanding mines. Recommendations will also be made for research on advan
control technologies based on criteria and needs determined by this progr

RESULTS

Two examples of program output -- control technology efficiency an
treatment costs -- are described in this report:

CONTROL TECHNOLOGY EFFICIENCY

Mine PA-1

Two mines in Pennsylvania, PA-1 and PA-3, serve as examples of
adequate and inadequate treatment. At mine PA-1, water from an active p
is pumped through a six-inch flexible vinyl hose for several hundred yar
to a flash mixer powered by the water velocity from the pump. The mixer
is housed in a small wooden shed. Approximately 50 pounds of hydrated
lime is manually added to the mixer every two hours. The mixer effluent
flows through a wooden sluice box into the first of three settling ponds.
Most of the sludge and sediment is retained in the first pond; retention
time for this pond is estimated to be approximately nine hours.

The values listed in Table 1 show the effluent limitations promul
by the EPA and adapted by the Office of Surface Mining Reclamation and

```
          ┌─────────────────────┐
          │ ENVIRONMENTAL IMPACTS OF │
          │ INDIVIDUAL MINE SITES    │
          └─────────────────────┘
                    │
                    ▼
              DOES COMPLIANCE
         WITH EFFLUENT GUIDELINES
   YES ───     PROVIDE ADEQUATE      ─── NO
              PROTECTION FOR PUBLIC
                  HEALTH?
    │                                    │
    ▼                                    ▼
┌──────────────┐              ┌──────────────────┐
│ RECOMMENDATION FOR │        │ RECOMMENDATIONS   │
│ STATUS QUO FOR     │        │ FOR LOCAL CHANGES │
│ LOCAL AREA         │        │ IN EFFLUENT GUIDE-│
└──────────────┘              │ LINES             │
    │                         └──────────────────┘
    │                                    │
    │     ┌──────────────────┐           │
    └────▶│ ASSESSMENT OF    │◀──────────┘
          │ REGIONAL         │
          │ ENVIRONMENTAL    │
          │ IMPACT (ALL SITES)│
          └──────────────────┘
                    │
                    ▼
          ┌──────────────────┐
          │ RECOMMENDATIONS   │
          │ FOR GENERAL/REGIONAL│
          │ CHANGES IN EFFLUENT│
          │ GUIDELINES         │
          └──────────────────┘
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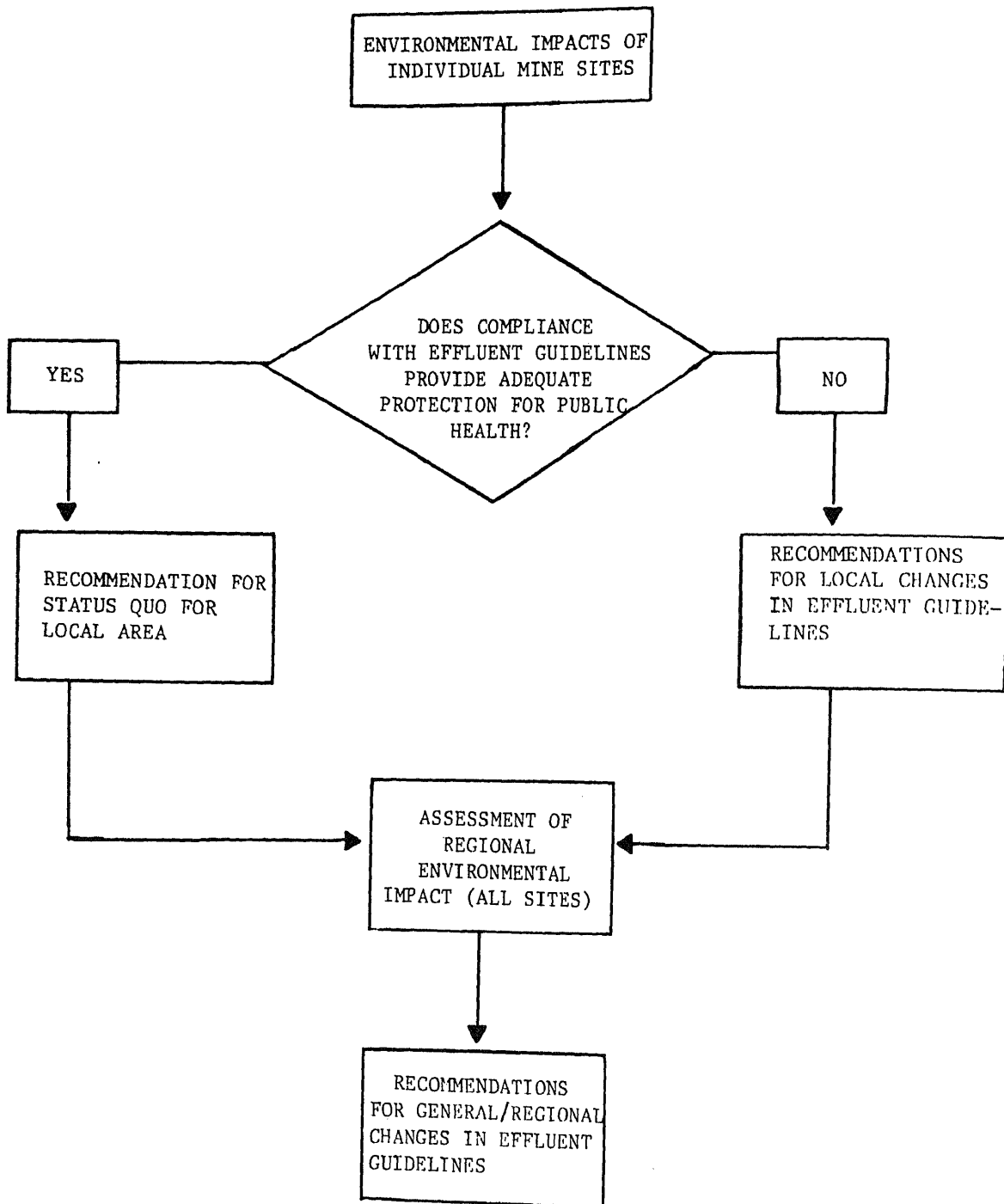
following treatment, data from the first settling pond outflow (B) indicate compliance (maximum allowable) was attained for the mean of all four parameters, although occasionally levels of suspended solids (three out of 23 visits) and manganese (three out of 22 visits) were in violation of the standards.

Data from the second settling pond outflow (C) show a lesser incidence of violating the maximum allowable standards.

In general, the effluent discharged from this site met the maximum allowable effluent limitations. The lime treatment was adequate and effective. There were occasions when pH, manganese, and suspended solids levels were not in compliance, a situation reflecting inadequate process controls since the operation is manually operated and controlled.

Mine PA-3

Water treatment at mine PA-3 consists of collecting pit water in a sump; adding an alkali reagent occasionally, but not necessarily regularly, then pumping the effluent into the first of three settling ponds. The alkali, soda ash (Na_2CO_3), is mixed by hand with pumped pit water in a 55-gallon drum that is perforated in its lower portion and base to allow the dissolved reagent to flow back into the sump. The water pumped into the settling ponds had minimal retention time as the ponds were nearly filled with solids, including coal fines. A secondary treatment, only occasionally used, consisted of a perforated bucket filled with soda ash briquettes or hydrated lime below the outflow of the first settling pond.

The values listed in Table 3 show the pit water (mean values for suspended solids, manganese, and iron and the range of values for pH) in violation of the maximum allowable standards for each of the four parameters. Following treatment some improvement was noted in all four parameters, but the mean values (B) still show the mine is not in compliance. Only once during the entire range of sampling dates was the pH raised to an acceptable level, but on this date the suspended solids reached 1800 mg/L indicating only partial treatment, poor settling sludge characteristics, and probably inadequate retention time. Iron levels in the first pond were in compliance on less than half of the sampling dates, suspended solids 60% of the time, and manganese only 10% of the time.

Effluent from the final settling pond outflow (C) was in compliance only for mean values for suspended solids; although minimal improvement was noted, mean values for pH, iron, and manganese were still in violation of the guidelines. For the final effluent leaving the mining site, violation of standards for suspended solids occurred on 20% of the sampling dates, for iron on 70% of the dates, and for pH and manganese on over 90% of the dates.

Effluent	Maximum Allowable	Values for 30 consecutive discharge days
pH[a]	Within range of 6.0 - 9.0	
Total suspended solids[b]	70.0	35.0
Iron, total	7.0	3.5
Manganese, total[c]	4.0	2.0

[a] Where the application of neutralization and sedimentation treatment technology results in inability to comply with the manganese limitations set forth, the regulatory authority may allow the pH level in the discharge to exceed to a small extent the upper limit of 9.0 in order that the manganese limitations will be achieved.

[b] Limitations given are for eastern and midwestern states. Western states are treated on a case-by-case basis, but levels must not be greater than 45 mg/L (maximum allowable) and 30 mg/L (average of daily values for 30 consecutive discharge days) based on a representative sampling.

[c] The manganese limitations shall not apply to untreated discharges which are alkaline as defined by the EPA (40 CFR 434).

Effluent	Standard		Mean	Min.	Max.
pH				6.3	8.8
				4.2	8.7
Total suspended solids	70 mg/L	A.	162.4	14.0	1380.0
		B.	39.3	4.0	203.0
		C.	14.6	0.0	124.0
Total iron	7.0 mg/L	A.	4.1	0.0	14.0
		B.	1.0	0.0	3.8
		C.	0.5	0.0	2.8
Total manganese	4.0 mg/L	A.	5.3	1.2	29.2
		B.	2.4	0.5	4.2
		C.	1.7	0.2	3.7

Note: A. Pit water, 26 samples.
       B. First pond outflow, 23 samples (Note: 22
          samples for manganese).
       C. Final pond outflow, 26 samples.

Table 3. Mine PA-3 (Units in mg/L except pH)

Effluent	Standard		Mean	Min.	Max.
pH				3.2	5.9
				3.5	8.5
				2.9	6.7
Total suspended solids	70 mg/L	A.	185.6	0.7	2600.0
		B.	2544.6	5.0	43350.0
		C.	58.7	3.0	380.0
Total iron	7.0 mg/L	A.	21.2	2.6	110.0
		B.	16.9	0.1	94.0
		C.	12.8	0.1	41.3
Total manganese	4.0 mg/L	A.	12.0	1.1	27.0
		B.	15.3	1.5	28.0
		C.	15.1	3.1	27.0

Note: A. Pit water, 24 samples.
       B. First pond outflow, 18 samples.
       C. Final pond outflow, 24 samples.

with solids and channels developed which... through the ponds, resulting in negligible retention time for flocculation and settling of solids. Often the suspended solids concentration increas... between the pit water and the final settling pond.

TREATMENT COST FOR MINE PA-1

Since mine PA-1 is conscientiously attempting to comply with the effluent limitations guidelines, an examination of its most recent treatm... cost data gives an indication of the level of costs that the industry fac... in maintaining compliance.

Mine PA-1's operation ultimately will affect 100 acres, 95 of whic... contain coal. The average coal thickness is 3'1" and, at the standard ra... of 1800 tons/acre ft of coal, each acre contains approximately 5600 tons of coal. At a recovery rate of 90% for surface mined coal, this mine wil... produce 478,800 tons of coal (95 acres x 5600 tons/acre x 0.9 [recovery] 478,800 tons).

In order to control the sediment related to the mining, storage po... and diversion ditches need to be constructed and, after mining ceases, re... and reclaimed. The sediment collected in these ponds during the mining operation must also be removed and handled in a manner consistent with environmental standards. The following costs and assumptions were based on discussions with on-site company personnel. These costs are life-of-mine costs and are related to the total tonnage the mine is expected to produce.

Sediment Control

1. Pond Construction

   Sediment storage: 0.2 acre ft/acre of disturbance x 100 acres disturbed = 20 acre ft.

   Storm water storage (10 yr - 24 hour storm): 4" rainfall x 0.5 (runoff coefficient) x 100 = 17 acre ft.

   Total capacity needed = 37 acre ft.

   Plan: 3 ponds, 12-15 acre ft. each.

   Cost per pond:

Earthwork and seeding	$ 8,000
Discharge pipe	$ 1,500
Engineering and management	$ 4,000
Total	$13,500
3 Pond Total	$40,500

2. Sediment and Pond Removal

> Sediment removal: Assume 10 acre ft (16,100 cu yd of sediment)
> Removal and disposal @ $2.50 cu yd = $40,250

> Pond removal = 1/2 of construction cost = $20,500.

3. Diversion Ditches

> 9000 ft @ $2.50/ft = $22,500.

> Removal = 1/2 of construction cost = $11,250.

> Total = $33,750.

> Note: 6500 ft of ditch built under old law specifications
> exists. Estimated cost of that ditch, 6500 ft x
> $1.50/ft = $9,750. New cost under new law = $24,000.

Summary of Sediment Control Costs

Pond construction	$ 40,500
Sediment and pond removal	$ 60,750
Diversion ditches	$ 24,000
Total cost	$125,250

Cost/ton – $125,250/478,800 = $0.26/ton.

The water treatment costs were provided by the company following its investigation of compliance costs for a recent six-month period in 197 to meet the new effluent limitations. The mine has complied with most effluent discharge criteria except for periodic violations of the manganes limitation. Production was 65,000 tons for the six-month period.

Water Treatment Cost – Six-Month Period

Equipment and Power

Pumps, hoses, and misc.	$650/month	$ 3,900
Electric and fuel	$350/month	$ 2,100
Lime (100 tons)	$ 55/ton	$ 5,500

Ponds

3 @ 1.8 acre ft each pond		$ 1,800 each
Earthwork		$ 1,200 each
Seeding, mulching, misc.		$ 3,000 each
Total		$ 9,000

365 days/2 x 24 hr/day x $27.50/hr = $120,750

Engineering and Management

    15% of equipment and labor $21,700

Summary of Water Treatment Costs (Six Months)

Equipment and Power	$ 6,000
Lime	$ 5,500
Ponds	$ 9,000
Equipment and Labor	$124,450
Engineering and Management	$ 21,700
Total	$166,650

Cost/ton = $166,650/65,000 = $2.56/ton

Total sediment control and water treatment cost = $2.82/ton.

    The total cost of $2.82/ton is relatively low compared to costs at our other eastern sites because the affected area of the mine has rather shallow slopes. As the slope angle increases, our preliminary findings indicate a corresponding rapid increase in sediment control costs, with final costs often exceeding $7/ton. The costs presented for mine PA-1 still do not represent costs for total compliance, as the manganese stand is often violated. The company estimated an additional $0.65-$0.75/ton for full compliance.

CONCLUSIONS ON CONTROL TECHNOLOGY EFFECTIVENESS

    The major conclusion drawn from this survey of control technology at sites PA-1 and PA-3 and at other surface mines is that the ECT "state-of-the-art" is generally at a very low level. Related conclusions includ

1. At the present time, mine drainage control and treatment at surface coal mines may not reflect conscientious planning and engineering design work by mine operators. On the whole, control technology (including reagent application) may be haphazard and periodically inefficient. However, there are some notable exceptions.

2. Surface mine operators favor small, efficient, and above all, portable application systems for neutralization reagents. Because effluent discharge points at surface coal mines do not remain constant over long periods of time and because discharges are generally small (< 5 gpm) and variable, it is

install sophisticated, permanent treatment facilities.

3. When choosing a reagent to neutralize mine drainage, reagent cost per unit quantity is less of a deciding factor to surface coal mine operators than ease of reagent application and handling. Thus, small caustic soda (NaOH) and soda ash (Na_2CO_3) treatment systems are common, even though reagent costs (based on treating water of equivalent acidity) may be several times the cost of hydrated lime or limestone treatment.

4. There needs to be more pre-mining planning by surface mine operators to develop mining methodologies which minimize pyrite oxidation and hydration. Some additional investment in exploration plus a prudent choice of a mine plan, drainage plan, and reclamation plan may minimize the generation of poor quality effluents. Mine operators may thus realize economic benefits from minimal initial investments which prevent the generation of poor quality effluents, as opposed to the operators' maintaining treatment facilities during and after mining, a long and costly process.

5. Costs for compliance with EPA/OSM effluent limitations can range from $3-$7/ton. The higher costs are associated with steeply-sloped terrain.

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1. INTRODUCTION

Coal from mines is transported to its ultimate destination by rail, barge or pipeline. Once it arrives at its consumption point or a process facility, it is moved over short distances by rubber-tired loaders, conv or rail shuttle cars. During the transportation process, the coal is oft exposed to the elements. This leads to dust emissions and losses throug effects. Moisture absorption and oxidation also can occur, causing deter tion of the coal and loss in fuel value (ERDA, 1976).

Once at the destination, the coal is either used or stored. Most us maintain stockpiles comprising a 90-day supply at their normal use rate. is done primarily to provide a reserve in the event of temporary loss of ply. This stockpile may stand for a year or more before it is necessary use it.

In the stockpile, the coal is subject to weathering and oxidation. dust emissions from stockpiles are common. Absorbed moisture from rain o causes leachate formation and may decrease the fuel value of the coal by 8% depending upon initial moisture level and coal rank. Wind and rain er results in coal migration and exposes new coal surface to weather. Moist can also freeze solid in cold weather making normal handling impossible. dation may reduce the heating value up to 5% over a one-year storage peri (ERDA, 1976). In addition, internal oxidation can lead to spontaneous c tion in low rank fuels (ERDA, 1975; Paulson, et al., 1975).

This work presented here addresses the use of protective coatings fo coal to resolve the environmental problems associated with transport and storage. These coatings not only reduce environmental pollution and impr handling characteristics, but can also be shown to provide dollar savings substantially greater than the costs of application.

2. TECHNICAL APPROACH

The overall objective of this work was to demonstrate the feasibilit economical coal coating systems. To accomplish this, the following facto were considered:

- Identification of suitable materials for coal coatings

- Development of formulations which are capable of reducing the adverse environmental effects of weathering of coal storage

- Identification of acceptable application techniques

- Tests to determine coating properties and provide data for economic analysis

- Evaluation of candidate filler-binder materials
- Review of current coal protection techniques
- Application considerations
- User motivation

Filler-Binder Materials Evaluation

A list of materials was generated which could be considered as candidate for inclusion in coal coating formulations. The candidate materials were screened to establish their characteristics with respect to:

- Cost
- Availability
- Fuel value
- Physical properties
- Environmental pollution potential

The filler materials considered included coal, paper, sawdust, bagasse, rice hulls, cottonseed hulls, and fly ash. Binder materials considered fall into two categories. The first included the materials useful for the hot-melt type of coating such as waxes and plastics. The second type of binder material was the various latex emulsions. This type of material was considered for use in filled latex coatings.

Pulverized coal and fly ash emerged as the best filler candidates. Both of these materials are available at coal user sites in sufficient quantities. They are both available at little or no cost, taking into account the credit for fuel value of coal. Neither of these materials would cause additional environmental problems upon combustion, as both are normally present in coal combustion systems. The other filler material candidates were either too costly, limited in availability or presented potential environmental problem. The best binder materials identified were slack wax, polyethylene, atactic polypropylene for the hot-melt composition, and polyvinyl acetate copolymers for the filled latex formulations.

Current Coal Protection Techniques

The most common current means of protecting coal is to carefully build and compact the stockpile, then monitor it for hot spots. At this time, it estimated that less than 5% of the users of coal provide additional protection in the form of coatings. Coal is shipped by rail car in as-dumped condition. It is estimated that 5-10% of the shippers use latex crusting compounds to prevent wind loss and dust emissions in transit. A discussion of these current protection methods is provided below.

Stockpile Formation

Large users of coal generally maintain a stockpile sufficient to provide coal for 90 days in the event of a strike or other loss of supply. A typical

within six days after pile formation (wilson, 1975). A typical method of constructing a coal stockpile is given below.

1. The coal is dumped from the rail cars either by bottom hopper c invention.

2. The coal falls onto a conveyor and passes through a mill where ground to <2-inch size pieces.

3. The coal is transported to the stockpile areas either by convey by rubber-tired vehicle.

4. A bulldozer spreads the coal and compacts it. Typical piles ar the form of a truncated cone, 100-200 feet wide at the base and 25-50 feet high. The length of the pile may be up to thousands feet.

Coal as dumped has a bulk density of about 50 lb/ft^3. After compaction, bulk density is about 65 lb/ft^3 (Paulson, et al., 1975).

The stockpiling technique varies with coal source and rank. Higher coal may be formed into larger piles of greater height and stored longer low rank coals (ERDA, 1975). East coast coals may be stored longer than coast coals as they are less reactive. The finer the coal, the more reac it is as a result of greater surface area.

Small coal stockpiles may be stored as dumped for short periods. Su piles should not exceed 15 feet in height (Wilson, 1975). Longer term stor of uncompacted coal is risky in terms of spontaneous combustion danger. Uncompacted coal piles should be used within a few days of dumping.

Stockpile Protection

Stockpiles are formed solely by the action of a bulldozer in shaping compacting the pile. Thermal probes are sometimes buried in the coal to m tor pile temperatures. The probes set off an alarm if the pile temperatur reaches 130-140°F (54-60°C).

Dust emissions from coal stockpiles are a problem of increasing conce Some users reduce dust formation by washing the coal before piling and tra porting it wet. Other users wet the pile after formation or spray it with to reduce dust emissions.

Leachate formation is also a serious problem except in the case of ve high grade coal. Water runoff from the pile is collected in a trough arou the pile. It is then sent to a holding tank or pond where it is treated b fore discharge to the environment. The treatment generally consists of in ducing a flocculant or precipitating agent, then allowing the solids to se out before discharge.

sultant fuel value losses. ERDA (1976) reports that losses up to 5% may occ[ur]
in the first year of storage. Leonard (1968) found that properly stored coa[l]
will lose only 1-2% per year of its energy value due to oxidation. However,
improper storage was found to result in losses of 3-5% per year.

Latex Crusting Compounds

The only protective coating of significance in current use is the latex
crusting compound. This material is essentially a paint base, and it is pro[-]
duced by paint manufacturers. Numerous small firms purchase this material a[nd]
resell it as a protective coating for coal or as a surface stabilizer for
earth, sand or other materials stored in stockpiles. The latex compounds ar[e]
normally applied after dilution by a factor of 3/1 to 20/1. They are spraye[d]
onto the material to be protected using any equipment capable of spraying wa[ter.]

Formulation and Evaluation of Coatings

During this work, 119 hot-melt formulations and 39 latex mixes were pro[-]
duced and evaluated. The types of tests conducted were as follows:

Visual observation	Viscosity
cracking tendency	Density
surface texture	Thermal expansion
adhesion to substrate	Water permeability
Compressive strength	Rheology
Tensile strength	Grindability

Not all tests were run on all formulations. Some tests, such as tensile an[d]
compressive strength, were run on a limited number of specimens to establi[sh]
the order of magnitude of the results. No means of converting strength dat[a]
into a useful parameter for characterizing the utility of coatings was iden[ti-]
fied. Thus, the data are of interest primarily as a means of estimating
cracking potential.

Other tests, such as water permeability, effects of thermal cycling and [co-]
efficient of thermal expansion relate directly to the quality of the coating[.]
Tables I and II summarize the results of these tests on formulations that we[re]
near the optimum compositions for both the hot-melt and filled latex coating[s.]

Test Panels

Those formulations which appeared to best meet the above criteria were
cast onto frames, 12" x 12", with about 3-4" of coal as a substrate. The
frames were constructed with wooden pegs spaced at 3/4" intervals around th[e]
periphery. The pegs served to restrain the coating from shrinkage to enhan[ce]
crack formation and present a more realistic test than would an unrestraine[d]
coating. The coating was applied in thicknesses ranging from 1/8" to 1/2".
Figure 1 shows two views of a test frame with a hot-melt coating in place.
Figure 2 shows a cross-section view of the coating on a coal bed.

The test frames were subjected to a "rainfall" test. In this test, th[e]
equivalent of 2" of rain was sprayed on the surface of the test panel. The

Table I. Physical Properties of Hot-Melt Formulations

ENTRY NO.	COMPOSITION	VISCOSITY Avg. KP RPM			TENSILE PROPERTIES (−30°F) At Rupture			COMPRESSIVE STRENGTH, (70°F) at Failure (PSI)	STRAIN IN COMPRESSION At Failure (%)	DENSITY GM/cm³ (70°F)
		1	2.5	5	Stress (PSI)	Strain (%)	Tangent Modulus (PSI)			
e-16-4	85.0% Coal 12.0% SW 3.0% PE							333 392 302 Avg 342	1.9 1.3 1.6	
e-17-1	85.0% Coal 12.0% SW 3.0% PE							248 278 249 Avg 258	1.8 2.1 2.1	
e-17-2	85.0% Coal 12.0% SW 3.0% PE							148 179 192 Avg 173	2.2 1.9 2.3	
6-2-3	77.5% Coal 14.9% SW 3.8% PP 3.8% PE	8	7	4	210 79	0.4 0.7	106,000 18,200			1.1
1-2	80.0% Coal 15.2% SW 2.4% PP 2.4% PE				222 233 241	0.4 0.6 0.5	84,800 68,200 83,600			1.08

W = Slack Wax
E = Polyethylene
P = Polypropylene

Table II. Characteristics of Hot-Melt and Filled Latex Compositions

REFERENCE NUMBERS	LEAK RATE, % OF SPRAY			36" Shrinkage	CTE STRIP Reheat Shrinkage	AVERAGE CTE	RESTRAINED ENDS GAP	GRINDABILITY
	70°F	+160°F	-30°F					
-1-2								
80.0% Coal 13.4% SW 3.3% PE 3.3% PP	3.3	8.1	11.0	0.335"	–	7.6×10^{-5}	–	Fair
-2-3								
77.5% Coal 14.9% SW 3.8% PE 3.8% PP	1.4	5.2	8.0	0.305"	–	6.6×10^{-5}	–	Fair
-1-2, 5-30-1								
80.0% Coal 15.2% SW 2.4% PE 2.4% PP	14.0	20.0	78.0	0.285"	0.278"	6.2×10^{-5}	0.118"	Fair
8								
50.0% Coal 23.0% Vinyl acetate copolymer 27.0% Water	7.7	1.8	1.2					Good

W = Slack Wax
E = Polyethylene
P = Polypropylene
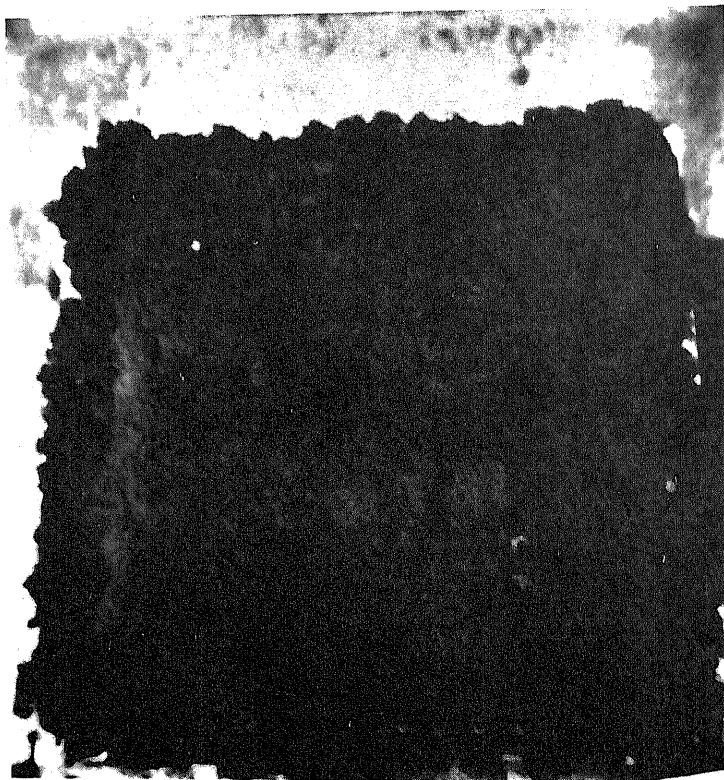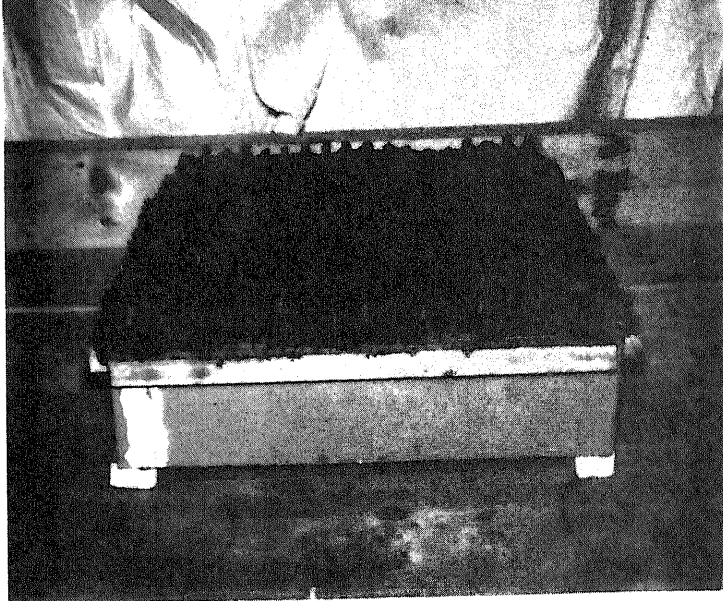
Figure 1.   Hot-Melt Coating on Test Frame

Figure

Thermal expansion or contraction is an important characteristic of ho
melt coatings. If the degree of contraction upon cooling exceeds the stra
to-failure of a coating material, cracking will result. Similarly, if the
thermal expansion upon heating exceeds the compressive strain-to-failure,
coating will shatter.

The coatings listed exhibited Coefficients of Thermal Expansion (CTE)
ranging from 6×10^{-5} to 14×10^{-5} in/in°F. Thus, for a 100°F temperature
change, the degree of expansion or contraction would be about 0.6% to 1.4%
The tensile strain to failure was measured to be about 0.5%. Thus, most o
ings would be expected to crack upon cooling by 100°F or more. Heating do
not appear to be a problem. Compressive strain-to-failure was measured to
about 2%, and none of the coatings tested expanded that much.

The CTE is not the only factor in cracking of the hot-melt coatings.
materials were generally cast at 200-250°F. In general, the coatings rema
fluid until they cooled to below 200°F. They then start to shrink, if unr
strained. Total shrinkage upon cooling to 70°F ranged from 0.6% to 1.7%.
cooling behavior was a function of the composition, however. The CTE curv
for typical compositions are shown in Figures 3 and 4. Formulations with
values similar to that shown in Figure 4 would probably be satisfactory fo
stockpile applications.

Latex Formulation Results

A total of 39 latex formulations were prepared and evaluated during t
work. Included in this number were four tests of commercially available l
crusting compounds for comparison purposes. The remainder of the formulat
were filled latexes, in which pulverized coal was used as an extender to i
prove the waterproofing character of the latexes.

Some of the latexes tested were not compatible with coal. In the prese
of coal, they coagulated or solidified rapidly. Daratak SP-1065, Everflex
and DLR-H resins yielded satisfactory coating films. All others tested we
incompatible with the coal.

The probable reason for the observed incompatibility is de-emulsifica
of the resin by chemical reaction with ionic components of the coal. Anot
possibility is instability resulting from pH change because of acidic sub-
stances in the coal.

Filled latex coatings made with polyvinyl acetate resins were applied
1-ft x 1-ft panels similar to those previously described for the hot-melt c
ings. All of the coatings were leakers in the "rainfall" test. The best o
these coatings was an Everflex GT mix with 50% coal, which exhibited only a
13% leak rate.
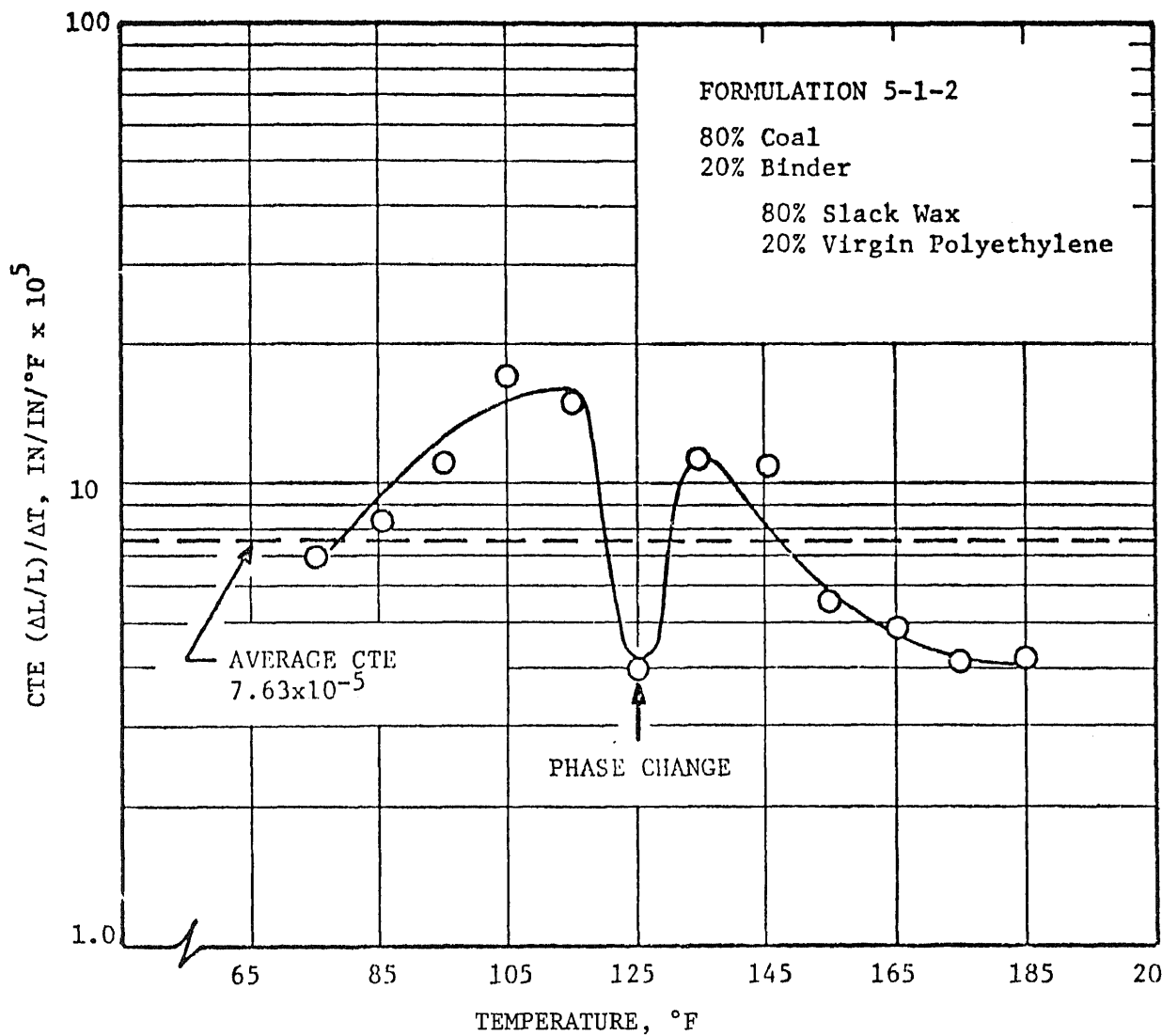
Figure 3. Coefficient of Thermal Expansion Curve for Formulation 5-1-2
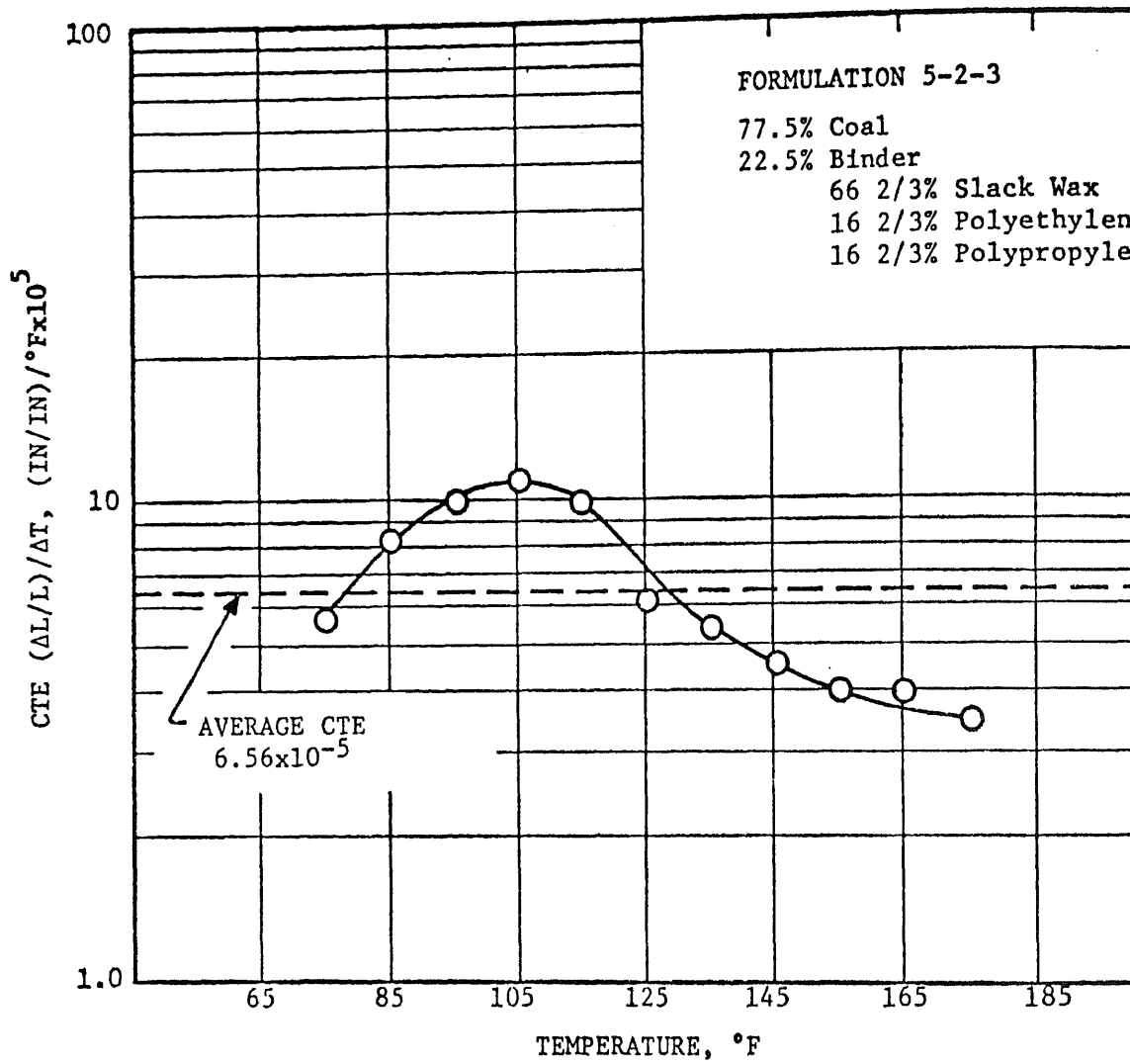
Figure 4. Coefficient of Thermal Expansion Curve for Formulation 5-2

50-90% of the "rainfall" water penetrated the coating. The filled latex coating did form a cohesive film on the surface, however. Less than 8% of the "rainfall" water ahdered to the surface or passed through the coating, even after exposure to a temperature range of -30°F to +160°F. In the economic analysis, presented later in this paper, filled latex coatings on bot normal and specially prepared surfaces are considered for comparison purpos

Tests on commercial latex crusting compounds showed that they do not p vide a significant degree of waterproofing to coal. The minimum leak rate noted was 78%. One commercial product was tested at the recommended concen tration and again at 5 times the recommended amount. The leakage rate was similar in both cases. The unfilled latexes cannot be considered as a sati factory waterproofing agent for coal stores even when applied at substantia higher levels than recommended by the manufacturers for dust control and su face stabilization.

Application Techniques

Application experiments were conducted to assess characteristics of ho melt materials. The principal objective was to assure that the materials could be pumped without problems due to viscous effects or vapor lock. Ini tial experiments showed that compositions containing 80% coal were easily transported through a one-inch diameter tube. Flow was initiated with less than 2 psig pressure differential.

A system capable of applying hot-melt materials comprises the followin elements:

a)	Crusher/grinder	f)	Slurry pump (heated)
b)	Polymer melt vessel	g)	Service lines (heated)
c)	Coal preheater	h)	Steam boiler
d)	Metering system	i)	Dispensing system
e)	Mixing vessel (heated)		

A schematic of the system is shown in Figure 5. As shown, a mixing vessel is included in the current subscale apparatus. This mixer is used a a batch heater and dispenser. For larger-scale applications, a continuous system would be more desirable.

Hot flow application resulted in an excellent layer of coating on an i clined 4 x 8 foot panel. The material thickness varied from 1/8 to 1/4 inc thick. Figure 6 shows a technician in the process of coating a 4 x 8 foot pa

3. ECONOMIC ANALYSIS

The following section is an evaluation of the costs and benefits which would accrue from the use of protective coatings for coal. Uses of latex crusting compounds, filled latex coating and hot-melt coatings are consider
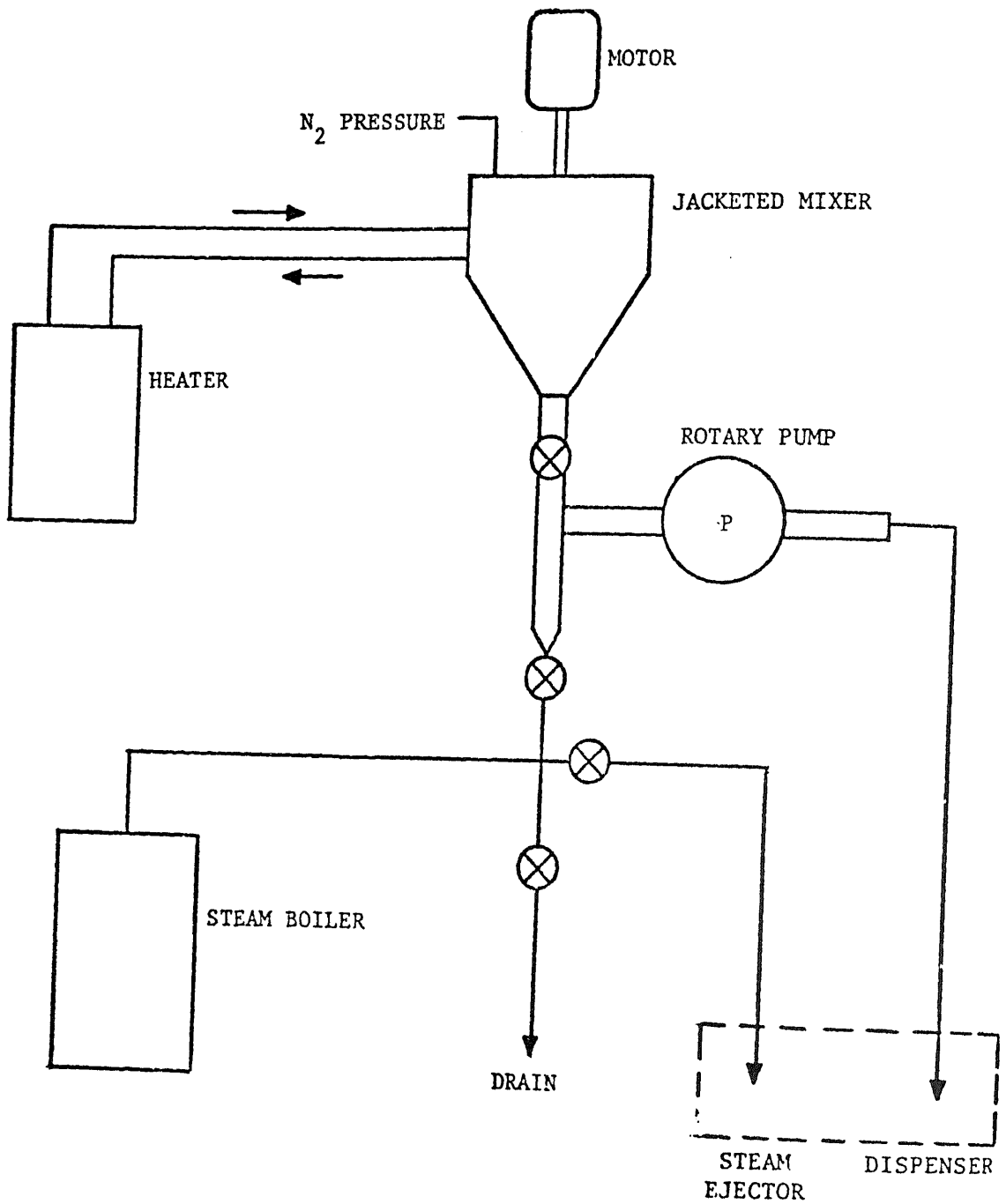
Figure 5. Schematic Diagram: Coal Cover Application System
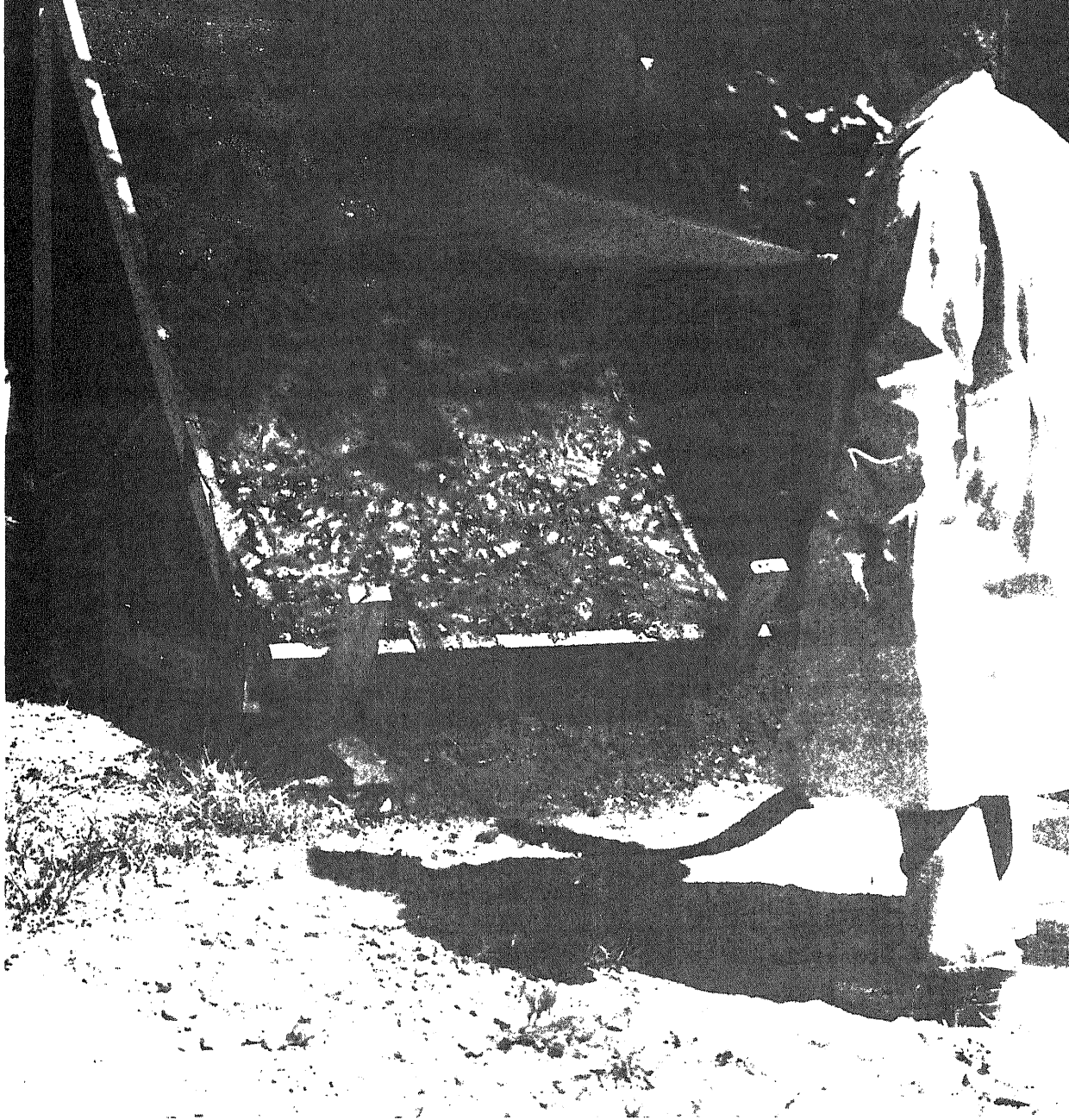
Figure 6. Application of Hot-Melt Coatings

Table III. Coal Beneficiation

Dump coal from cars
Grind to <2 inches   ⎫
Transport to pile   ⎬ Current practice, unprotected piles
Unload on pile   ⎪
Form and compact pile   ⎭

Latex Crust	Filled Latex	Hot Melt
1. Mix with water, 3-10/1	1. Grind coal for surface preparation*	1. Grind coal for coating mix
2. Spray apply 4-11 gal/500 ft^2	2. Grind coal for coating mix	2. Prepare wax/plast binder
	3. Mix coal, water, latex	3. Heat and mix components
	4. Spray apply 7-31 gal/ 500 ft^2	4. Spray apply 20-8(gal/500 ft^2

* optional

Summary of Stockpile and Rail Car Protection Costs

Table IV shows a summary of the costs of building and protecting a coal
stockpile. A 250,000 ton stockpile was used as a basis for comparison.
Table V is a summary of the costs of various techniques for protecting coal
in rail cars.

Table IV. Summary of Stockpile Protection Costs
Basis: 250,000 ton stockpile

Treatment	Time Required Days	Total Cost $	Cost/to $
Build and Compact Stockpile	50	55,000	0.22
Monitor Stockpile for 1 year	365	22,750	0.091
Latex Crusting Compound, 1 gal/200 ft^2	3.5	8,400	0.034
Filled Latex on Surface Fines, .025"	13.3	19,500	0.078
Filled Latex on Surface Fines, .050"	26.6	25,908	0.107
Filled Latex on Surface Fines, .100"	53.2	42,000	0.168
Filled Latex on Normal Surface, 1/8"	11.7	33,506	0.134
Hot-melt on Normal Surface, 1/8"	11.17	12,788	0.051
Hot-melt on Normal Surface, 1/4"	23.4	25,576	0.102

Treatment	Total Cost $	Cost/Ton $
Latex Crusting Compound, 1 gal/500 ft^2	700	0.07
Filled Latex on Surface Fines, .050"	3,844	0.38
Filled Latex on as Dumped Surface, 1/8"	4,320	0.43
Holt-melt on as Dumped Surface, 1/8"	1,355	0.14

Cost/Benefit Analysis - Stockpile Applications

This section illustrates the benefits to be derived from coal protecti
and the estimated return on investment. This analysis is based upon protec
tion of a 250,000 ton stockpile for a period of one year. The value of the
coal is assumed to be $20 per ton.

The cost factors used in determining treatment costs are listed below.

	Cost, $/Ton
Build and compact pile	0.08
Apply latex crusting compound	0.034
Apply filled latex coating, 0.025"	0.087
Apply hot-melt coating, 1/8"	0.051

The benefit factors used in determining the return on cost of applying
particular coatings are:

Reduce or eliminate dust emissions.
Reduce or eliminate leachate formation.
Maintain or reduce moisture content (fuel value effect).
Minimize freezing of coal into large agglomerates.
Prevent increase in moisture content (grinder operation).
Prevent stockpile migration.
Reduce or eliminate oxidative energy loss.
Reduce or eliminate spontaneous ignition.
Prevent wind or rain erosion.
Reduce need for snow removal.
Reduce monitoring costs.
Reduce fire prevention and extinguishment requirements.

The basis for determining the dollar value or equivalent for these benefit
factors is described in Kromrey, et al., (1978). The results are summarize
below. From this summary, the highest return per unit cost occurs by use o
the hot-melt formulation, i.e., return of benefits valued at $1.90 per ton
a cost of 13.1¢ per ton.

Compaction	0.06		
	0.114	0.65	1.09
Latex Crust*		1.04	1.65
Filled Latex Coating*	0.158	1.04	1.90
Hot-melt Coating*	0.131		

* includes compaction

Cost/Benefit Analysis - Rail Car Applications

This section illustrates the benefits to be derived for protection o[f]
coal in rail cars and the estimated return on investment. The results ar[e]
based upon protection of a unit of 100 cars containing 100 tons each of c[oal.]
The value of the coal is assumed to be $20 per ton. The benefit factors c[on-]
sidered are listed below:

> Reduce or eliminate dust emission.
> Reduce wind losses.
> Prevent moisture increase (fuel value effect).
> Prevent moisture increase (grinder operation).
> Prevent freezing of coal into large agglomerates.
> Reduce or eliminate spontaneous combustion.

Again, the basis used to convert these factors into an equivalent dollar
value is described in Kromrey, et al. (1978). The results are summarized
below. This summary indicates the benefit return per unit cost to be hig[h]
for the latex crusting compounds with $.74 per ton in benefit value result[ing]
from costs of $.07 per ton. For rail car applications, the latex crust ap[-]
pears to be most cost-effective.

Treatment	Treatment Costs, $/ton	Direct $ Savings, $/ton	Total Benefit Value, Equivale[nt] $/ton
Latex Crust	0.07	0.54	0.74
Filled Latex Coating	0.38	0.61	0.81
Hot-melt Coating	0.14	0.61	1.01

4. CONCLUSIONS

Based upon the results of this technical effort, the following conclu[-]
sions are presented:

1. Commercially available latex resins used as coal crusting compou[nds]
   can prevent dust loss and wind erosion, but do not waterproof th[e]
   coal surface.

2. Hot-melt formulations consisting of about 77.5% coal, 15% slack
   wax, 3.75% polyethylene and 3.75% polypropylene are capable of
   sealing a coal surface against water penetration.

resin and 2% water is capable of sealing a coal surface against
water penetration provided the surface is coated with fines of
less than about 1/8" particle size.

4. Hot-melt coatings appear to be most cost effective for application
   to coal stockpiles.

5. Latex crusting compounds appear to be the most cost effective means
   of protecting coal in rail cars.

6. The anticipated return in dollars and intangible benefits by use
   of the coal protection methods described herein is in the range
   of 10-15 times the cost of such protection.

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ABSTRACT

Enhanced oil-recovery processes are still developing. The transition from pilot testing to full-scale field application depends upon the success of field research that may improve the economy of enhanced oil-recovery processes. Underlying all development and expansion activities associated with oil production is the constant need to protect the environment from pollution. Unanswered questions regarding the environmental consequences of enhanced oil-recovery activities should be addressed during the period of pilot field testing.

Oil displacement by injection of brines (the waterflood process) entails the surface processing of large quantities of saline waters creating the potential for pollution of surface waters and shallow freshwater aquifers. Improved waterflooding techniques involve the introduction of surface active agents (detergents), caustics, and organic polymer compounds (particularly polyacrylamide), thus increasing the potential for pollution. It is increased further by the micellar-polymer process since the micellar solution is a mixture of surfactant, oil, water and a cosurfactant (usually an alcohol).

Enhancement of oil production by thermal methods adds another dimension to the environmental hazards through air pollution from steam generators and the produced fluids.

Other field operations, such as drilling and renovation of wells, create local environmental hazards, but these are becoming regional concerns as the search for new oil and the reactivation of old oilfields accelerates. This paper presents the potential pollution hazards of the enhanced oil-recovery processes and the environmental surveillance program being instituted by DOE.

INTRODUCTION

We are safe in predicting that the future will bring with it a greater population density. To maintain our standard of living, engineering technology will have more stringent demands

placed on it to provide the materials and utilities that go into
making life comfortable and healthy. However, in filling con-
sumer needs, engineers cannot ignore the ecological consider-
ations of every technological process. Governmental controls,
economic considerations, and diminishing resources have forced a
complete re-evaluation of waste effluents from all industries.
Waste must be negligible for the sake of the economy as well as
providing safety within the environment in which we live.

Enhanced oil-recovery processes are still developing. The
transition from pilot testing to full scale field application
depends on the economic success of field research. Underlying
all development and expansion activities associated with oil
production is the constant need for protecting the environment
from pollution. Unanswered questions regarding the environmental
consequences of enhanced oil-recovery (EOR) activities should be
addressed during the period of pilot field testing, now in pro-
gress. Environmental data can be obtained from pilot projects so
that discharges can be correlated over time with reservoir
characteristics and process variables for use in planning field-
wide commercial implementation of any process.

Potential adverse environmental concerns are enhanced by the
injection of large quantities of chemicals to displace oil in
producing wells. New chemical processes for oil recovery require
surface processing of large quantities of saline waters as well
as chemical mixtures. The large volumes of fluids create a
potential for pollution of surface waters and shallow freshwater
aquifers. When the oilfield is finally abandoned large quantities
of chemicals used for oil displacement will be left in the under-
ground reservoir, creating a potential for long-term environ-
mental hazards.

The United States Congress and State Legislatures have
enacted laws intended to protect our environment from pollution
due to human endeavors. Several of these laws have a direct
bearing on enhanced oil recovery, the most significant of which
are the Clean Air, Federal Water Pollution Control, and Safe
Drinking Water Acts.

Research with chemicals intended for use in enhanced oil
recovery is the best way to avert adverse environmental effects.
The Department of Energy has initiated several research projects
to examine the biological and chemical degradation of EOR chemi-
cals, the effects of injected chemicals on geologic strata,
toxicity of chemicals, water availability, and the socio-economic
aspects of enhanced oil recovery. This paper is a general over-
view of the environmental concerns of the enhanced oil-recovery

Plan for Oil Supply (2), prepared by the Department of Energy, provides a detailed analysis of the environmental concerns of oil production in the United States. A Programatic Environmental Impact Statement on the enhanced oil-recovery activities of the Department of Energy, which is now being prepared, will address specific aspects of developing technology.

Concern for the environment means that we do not wish to produce any kind of adverse effect on the air, water or soil by our activities. Therefore, the processes being used today for production of oil, as well as the new enhanced oil-recovery methods being field tested, are discussed from the viewpoint of their potential for adversely affecting air, water and soil. I is important to emphasize that the current EOR field activities of DOE are nothing more than research experiments. The cost-shared field testing program with industry is designed to evalu the utility, demonstrate the feasibility, and improve the tech-niques of the best technology presently available for productio of oil remaining locked in the ground after secondary recovery. In pilot experiments, the environmental impacts are confined to widely scattered, isolated local sites. We tend to lose sight this in considering the national concern over possible adverse environmental impacts from any activity. Although this report addresses the environmental aspects of EOR, it is a projection the hypothesis that the demonstration experiments now under way will prove to be successful and result in large-scale commercial ization of the EOR processes. By closely examining the pilot studies and looking ahead to commercial implementation, we hope to foresee any adverse impacts of EOR and alleviate them so commercialization can proceed in a timely manner.

EOR PROCESSES AND ENVIRONMENTAL CONCERNS

Secondary Oil Recovery

Secondary recovery (waterflood process) is conducted by injecting treated produced brines into oil-bearing strata to displace the oil to production wells. The brines are treated fo removal of iron and suspended solids, and, after filtration, a small amount of sodium bisulfite is added to removed entrained oxygen. Sodium tripolyphosphate is then added to prevent scale formation in the pipes. The addition of the sodium bisulfate an tripolyphosphate is a simple process and the concentrations used are so small that no environmental hazards exist from their use. The accumulation and processing of large volumes of oilfield brines does present serious potential environmental problems,

oilfields of five major oil-producing states (1) was that, from
the interpretation of chloride analysis, no pollution could be
attributed to oil and gas-field brine-injection operations.

On the average, only about 30 percent of the original oil-
in-place is produced by primary and secondary recovery methods.
The remaining 70 percent of the oil in the ground is the target
of tertiary recovery, or enhanced oil recovery, because this
resource is estimated to be greater than 300 billion barrels of
oil.

Chemical Flood

The two EOR processes that employ, and are based upon, the
technology developed for secondary recovery are known as Chemical
Flooding (or Improved Waterflooding), and the Micellar-Polymer
Process. Chemical Flooding, as the name implies, involves the
addition of chemicals to the brine prior to injection. At present
three types of chemical compounds are in the forefront of chemical
flooding. These are caustics (sodium hydroxide, sodium silicate,
ammonium hydroxide, etc), detergents (alkyl aryl suflonates), and
polymers (polyacrylamide and polysaccharide). A large body of
experience has already been accumulated in the use of polymer
solutions in oilfields, since more than 100 fields have been
treated with polymers of various kinds.

The construction of additional facilities (mixing tanks,
storage tanks, pumps, pipes, etc.) are necessary to mix and
process the chemical solutions at the field site: however, these
additional facilities are not very much different from those used
in routine oilfield operations. Large quantities of chemicals
will be injected over a long period, but it is not necessary to
store large inventories of chemicals at the field site. Hence,
the potential for environmental damage from storage and operation
of the facilities is confined to a small area of the field and
is limited to spills or leaks of less than the capacity of a
railway car or truck. Precautions against health hazards to
personnel using the chemicals in the field must be taken since
all of the chemical compounds are severe irritants to mucous
membranes.

Chemical compounds produced with the brine and oil are not
a cause for concern because only a small fraction of the injected
chemical is eventually produced. The amount of chemical injected
in a chemical flood is designed to be approximately equal to the

processed as a part of the crude oil. Any produced brine is
disposed of by injection into a nonproducing brine aquifer abov
or below the oil zone when it cannot be used in the brine injec
tion program.

The major potential environmental problems associated with
chemical flooding are: (1) Local air pollution by hydrogen
sulfide removed from the produced brine during treatment, (2)
Spills or leaks of chemical additives during transportation,
storage and processing, (3) Health hazards from the dry chemica
and solutions, to personnel operating the field, (4) Leaks from
surface storage and treatment ponds for produced brine, (5) Leak
from high-pressure pipes transporting mixed chemicals to the
wells, (6) Underground leaks into shallow aquifers from damaged
or corroded wells, (7) Production into shallow aquifers from
improperly plugged abandoned wells (possible when the pressure c
the oil reservoir is raised due to EOR activities,) (8) Producti
into aquifers above the oil reservoir through an incompetent sea
above the reservoir (fracture or fault), (9) Subsidence along a
fault plane caused by increase in reservoir pressure and (10)
Subsidence caused by chemical disaggregation of the oil reservoi
rock matrix.

Micellar-Polymer Process

The micellar-polymer EOR process involves four separate
phases of fluid injection beginning with a "preflush" injection
of fresh or low salinity water, necessary to adjust the salinity
and pH of the reservoir. The microemulsion is composed of a
hydrocarbon, brine, surfactant, co-surfactants (generally alcohol
and electrolytes. The third injected fluid is a polymer solutio
whose increased viscosity assists in more efficient displacement
of the oil bank and the microemulsion. Brine injection follows
the polymer solution as the fourth fluid-injection phase.

Although the micellar-polymer process is considerably more
complex, the environmental concerns are the same as those expres
for chemical flooding. The application of the micellar-polymer
process increases the need for surface equipment and requires
additional transportation, storage and a larger variety of
chemical compounds. During the injection of chemicals (the
second and third phases mentioned above) a large amount of
chemicals will be injected in a relatively short time when
compared to chemical flooding. Therefore, large inventories of

chemicals are required at the field site and several environmental concerns are intensified, but no new ones are added. Health hazards to personnel become greater because larger quantities of chemicals must be processed. Any leaks from surface storage or pollution of shallow aquifers from abandoned or incompetent wells going undetected for a long period would result in severe damage to ground or surface streams. However, recognition of intensified environmental concerns should result in more stringent design specifications of equipment and closer surveillance of operations. If abandoned or improperly plugged wells are suspected, monitoring of any fresh water aquifers along the hydraulic gradient during the chemical injection phases will be necessary.

In field tests of chemical flooding and micellar-polymer processes conducted so far, low-salinity water is used at various stages (preflush, surfactant solutions, polymer solutions, etc.). However, the trend is to design systems less sensitive to salt content and perhaps compatible with the produced oilfield brines. If this trend does continue and chemical solutions can be prepared in brines supplied by a brine aquifer and the oil reservoir, the presently foreseen socioeconomic impact of freshwater demand will be alleviated. If it is not possible to use oilfield brines for all of the chemical solutions by the time EOR processes are developed on commercial scales, a close analysis of water availability and negotiations for allocation will be required prior to implementation.

Thermal Processes

Three types of thermal processes have currently gained widespread recognition: (1) the steam soak process, (2) steam drive, and (3) in situ combustion. Processes using steam are viable commercial enterprises for viscous oils in California where approximately 250,000 barrels of oil are produced each day by steam injection. DOE will soon conduct some pilot field studies in the mid-continent region to use steam for enhancement of oil recovery from deeper, less viscous oils than those of California.

Steam Soak: This process involves the injection of steam for 10 to 30 days, followed by a shut-in period to allow for heat transfer and penetration of the steam. The wells are then opened for the production phase of the process, which may last as long as 6 months. The actual duration of the periods of injection, soak and production depends on the characteristics of the oil, formation, and experience of the operator.

wells. Oil is displaced to the production wells by a combination
of in situ distillation, solvent extraction by the advancing
products of distillation, and gas expansion. Condensation of
steam produces a zone of hot water that behaves as a hot water
flood. The maximum anticipated oil recovery from the commercial
projects now in progress is about 50 percent of the reservoir
in place.

Environmental Aspects of Steam Stimulation: The steam
processes require a constant source of fuel to generate steam
along with an ample source of fresh water. Crude oil produced
from the field, natural gas, processed fuel and coal are used for
steam generation based on availability, economics, and air pollu-
tant emissions. Water requirements depend upon the process in
use, total amount of steam required, and the ratio of the amount
of injected steam (as equivalent amount of water) to the amount
of oil produced, which may range from 0.1 to 5.0, or more. Steam
requirements gradually increase as depletion occurs.

The actual pollutant emissions from steam generation depend
on a large number of variables such as the type of fuel and its
chemical composition, the efficiency of heat exchange, design of
the boilers and stock, and meteorology. If produced oil is used
for fuel, approximately one-fourth of the production is consumed
in producing steam. Emissions from a 50MM Btu/hr boiler may
include: SO_2 (10-25 kg/hr), NO_x (2-10 kg/hr), solid particulate
(1-3 kg/hr), unburned hydrocarbons (0.2-0.5 kg/hr), and CO (0.5-
1.0 kg/hr). These are very broad ranges, but it is not possible
to present exact figures without measuring a specific installation
over a long period. However, one can realize from the data that
steam stimulation processes add a potential, and real, air-
pollution hazard arising from direct-fired boilers. Since the
total amounts of these pollutants must be maintained below State
and Federal emission standards, the use of steam is constrained
by the particular environmental standards involved. Perhaps the
constraint could be lifted if the boiler flue gases can be com-
pressed and added to the steam line, or injected separately into
the oil-producing zone, to assist in production of the oil.

DOE has a contract with the Carmel Energy Co. to test such
a process in Kansas. The Vapor Therm process is designed to
recover heavy oil by injecting a mixture of gases and steam to
reduce the viscosity of the oil, dissolve carbon dioxide gas in
the oil, and increase the reservoir pressure. The hot combustion
gases (3,500° F) flow from the burners into a drum containing
water where steam is generated by direct contact of the hot
combustion gases with the water. The steam combined with the

combustion products is injected at the wellhead at 350°-650° F. In addition to its function as a steam generator, the water drum also acts as a scrubber for the combustion gases. The water removes corrosive components which are neutralized prior to injection of the steam. Many of the solid and corrosive components in the exhaust gas are trapped and neutralized in the steam drum. Although small amounts of the water in the steam drum must be removed regularly, atmospheric pollutants are almost entirely eliminated and beneficial results to oil production are obtained from injection of the combustion gases.

The demand for fresh water is a major consideration of steam-injection processes since water containing salts cannot be used because of severe, irreversible damage to the boilers. The steam is employed to improve the mobility of viscous crude oils that cannot be produced by other known techniques. Tests are also being designed to determine the feasibility of using steam-drive processes for enhanced recovery of less viscous oils in the mid-continent region. In all cases, the demand for water must be compatible with regional water availability to municipalities and agricultural interests; therefore, this is a major initial consideration for all proposed steam-injection projects. There are several other environmental concerns associated with steam-drive processes in addition to air emission from the boilers and the water demand. Large amounts of produced water must be separated from the oil, treated, and disposed of in accordance with existing state pollution-control regulations. Produced oil emulsions are frequently difficult to break and require special treatment for resolution. The entrainment of oil from oil-water separation and emulsion-breaking systems also requires close control because of the adverse effect it has on the water-disposal system. Provisions must also be made for disposal of solid wastes from scrubbers, boilers, tanks and flow lines.

In Situ Combustion: Several fire-flood pilot studies were made in the mid-continent region in the decades of 1950 and 1960, but at the time they proved uneconomical and did not attain commercial prominence. However, the pilot studies were very important in development of theories and technology unique to the process.

The in situ combustion processes are based on generation of heat within the reservoir by burning some of the oil in the reservoir. One procedure is simply the injection of air into a well followed by ignition of the oil and continued injection of air as the burning front expands radially around the well. Heat at the burning front (800°-1,200° F) produces steam, coke, distillation of the oil, thermal cracking of some of the heavy ends and pressure to move the front toward peripheral production

zone ahead of the burning front. One method that has gained
recent prominence is the wet combustion process. After the
burning front reaches a predetermined size, water is injected
place of air to act as a medium to transfer heat from the bur
out zone to the oil zone ahead. After an initial transfer of
heat as steam, the burned-out zone is cooled. Continued inje
of water results in a hot-water drive which reduces the visco
of the oil and furnishes the driving energy to move the oil t
the production wells. Other methods involving the transfer o
heat to the oil zone by water are employed, (such as alternat
injection of air and water) but detailed analyses of these ar
beyond the scope of this paper.

Air emissions from a well-designed in situ fire flood ar
minimal. The thermal cracking reactions at the hot combustio
front produce light hydrocarbons that may escape during produ
tion at the surface along with some carbon monoxide, carbon
dioxide and sulfur dioxide. However, the larger portion of t
compounds probably remain confined in the reservoir. NO_x pro
tion generally is absent because the lower burning temperature
does not favor their production.

Water produced with the crude oil can contain significan
quantities of metals and metal oxides dissolved in the acidic
waters. These can cause contamination problems through spills
and from leaks of the acid waters while they are being process
on the surface for subsurface disposal. The pH of the reservo
water may be lowered to 2.5, enough to cause severe corrosion
well casings in plugged (abandoned) wells and may lead to con-
tamination of other aquifers communicating with the fire-flood
oil reservoir through the corroded segment of the abandoned we

Gas Flooding

Any process employing, or producing, a gas has a potentia
for air pollution which may be local (confined to less than 5
acres) or regional (covering several counties, or an entire
state). Gas flooding is the introduction of gases, such as li
hydrocarbons and carbon dioxide, into the petroleum reservoir
improve oil-recovery efficiency through several theoretically
beneficial effects: (1) The injected gas increases the reserv
pressure, furnishing energy to drive the oil to production wel
(2) By dissolving in the oil it reduces the viscosity and dens
of the oil and improves the mobility (ease with which the oil

stantly available source of inexpensive gas must be near the oil-
field. Examples are a producing gas field or a gas-processing or
manufacturing plant producing one of the required gases as a by-
product. The gas can be transported to the field by pipeline,
truck or railroad tank car.

Transportation of the gases to the field by pipe, truck or
rail is under strict regulation by both State and Federal statute
An accidental spill, or large leak, from any of these sources may
cause severe local hazards including the possibility of a fire
or explosion, but dissipation and dilution in the atmosphere will
remove the hazard. One must also consider the fact that a viable
economic incentive exists for not losing the valuable commodity
being transported.

Water may be injected in large quantities in addition to the
gas requiring the treating and processing of large volumes
of water at the surface similar to operations of a secondary
recovery process. The water is obtained from the produced water
and recycled with added water obtained from a brine aquifer or
nearby source of surface water. The water is generally treated
for removal of solids, adjustment of pH, oxygen removal to
reduce corrosiveness, and bacteria growth.

Air emissions at the field will generally originate from
power facilities such as diesel or natural gas engines used in
generating electrical power. Some hydrogen sulfide may also
escape from the water-treating facilities. Other minor emissions
may originate from storage tanks, vapor-recovery units and heater
treaters.

The potential for surface or shallow ground water pollution
is the same as discussed previously for any field project pro-
cessing large quantities of brine at the surface for reinjection.
Stored or impounded brine may leak, field pipelines may develop
leaks, and well casings may crack or corrode during injection and
production operations causing ground-water contamination. The
potential of leaks and pipeline breaks have long been recognized
as a result of secondary oil production. Because of strict State
regulations, equipment design and constant monitoring, the
likelihood of leaks and spills during enhanced oil-recovery
operations is considered less than for conventional operations.

gases containing hydrocarbon and
sulfur compounds. The gases are separated from the oil and ma
be placed in a pipeline if the hydrocarbon content is sufficie
or it may be burned if the nitrogen and sulfur content will no
exceed ambient air-pollution standards, and the quantity produ
is not sufficient to be of commercial value. Finally, it may
compressed and injected into the formation from which it was
produced as a pressure-maintenance technique as well as for
disposal.

LEGAL ASPECTS

The Department of Energy has been mandated by law to asse
the environmental aspects of all EOR processes, and to assure
that the commercialized EOR technologies are environmentally
acceptable. The EOR projects are required to meet Federal, St
and Local laws, regulations and standards. In this context, t
laws are those regulations for the enforcement (by agencies su
as the EPA) of standards established under the laws.

The National Environmental Policy Act of 1969 (NEPA), PL
91-190, requires Federal agencies to consider the environment
all actions that may affect the environment and to prepare
Environmental Impact Statements for any major Federal actions
that have a potential for an adverse effect on our environment
To implement the act, NEPA established the Council on Environ-
mental Quality which presents guidelines to Federal agencies w
respect to policy, responsibilities, planning and response
elements, operations and coordinating instructions. DOE's NEP
implementation guidelines provide for an ongoing and continuous
environmental appraisal and review process, including the prep-
aration and publication of EIS.

The Clean Air Act and its amendments of 1970 and 1977 (PL
91-604 and Pl 95-95) vested implementation authority in the
administrator of the EPA. . Each state has the primary responsi-
bility for assuring air quality within the state. EPA is instr
ted to compile a list of air pollutants to which the Act applie
prepare air-quality criteria, and determine ambient air standar
for pollutants listed in the air-quality criteria.

EPA regulations implementing PL 91-604 include the Nationa
Air Quality Standards (NAAQS) Primary and Secondary Ambient Air
Standards specified for sulfur oxides, particulate matter, carb
monoxide, photochemical oxidants, nonmethane hydrocarbons, and
nitrogen oxide, and Performance Standards for petroleum refiner
and storage of hydrocarbon.

must do so by December 31, 1982. To achieve this goal, EPA is promulgating an emissions offset policy. Under this policy, no increase in emissions will be allowed unless there is a corresponding reduction in emissions from existing sources.

The Clean Air Act Amendments of 1977 allow states to prevent degradation of air quality by SO_2 and particulates where air quality is superior to the NAAQS. Under these provisions, states are allowed to classify their regions into three zones: Class I Regions (with very clean air) where only extremely small emission sources are permitted, Class II Regions where new sources with moderate emission sources are permitted, if the combined effects of all sources do not exceed the allowable increments of air-quality deterioration, and Class III Regions where emissions from new sources are allowed to the extent of compliance with the NAAQS. Since many of these regions have not yet been designated, it is difficult to determine whether EOR target regions will be subject to air-quality provisions that are too stringent, given the current environmental control technology for the processes.

New Source Performance Standards are also changing. For example, prior to passage of the Clean Air Act Amendment of 1977, EPA set a tentative deadline of February 1978 for proposing New Source Performance Standards for coal-fired boilers, which may apply to boilers fired by other fuels as well. The proposed standards cover particulate matter, sulfur dioxide, and nitrogen oxide emissions. Preliminary information indicates that standards will be proposed for small boilers which are the most common for EOR steam processes and are not currently regulated. Depending on how stringent the regulations are, new boiler installations may be required to add control technology not previously used at steam-injection sites. Similar regulations could also develop for other aspects of EOR processes as well.

The Federal Water Pollution Control Act provides the framework for regulation of waste-water discharge to surface waters. A National Pollutant Discharge Elimination System Permit is required under this act before waste-water discharge to surface waters from any source. The intent of the act and the discharge permits is to require use of the best technology economically available by 1983 and to attain and maintain receiving-water quality adequate to assure protection of public-water-supplied water used for agricultural and industrial operations, and the

Control Act include the discharge of oil, removal of spilled oil,
oil-pollution prevention, and the National Pollution Discharge
Elimination System covering discharge permits and certifications.

A major objective of the Federal Water Pollution Control Act
was to prevent the discharge of pollutants into navigable waters,
the contiguous zone and the oceans. The discharge of oil is
prohibited, but under the provisions of the act pollutants do
not include the injection of water, gas and other materials into
wells to facilitate production of oil or gas. The regulation of
oilfield operations is left to authorities within the oil-
producing states. Therefore, the various states retain control
of the injection of fluids in enhanced oil-recovery operations.

EOR activities may be regulated under the auspices of the
Safe Drinking Water Act. Enhanced oil and gas-recovery processes
are given special consideration under this act. The law states
that Federal regulations for the state underground injection
programs may not prescribe requirements which impede any under-
ground injection for the secondary or tertiary recovery of oil
and natural gas, unless such a requirement is essential to
assure that underground sources of drinking water will not be
endangered.

Although there are no Federal statutes, state water-use
laws may present severe constraints to EOR development. Western
states water riparian laws are aimed toward defining allocations
for usage of the water resources. In essence, fresh water is in
limited supply and competing demands for it must be addressed
through this system.

The Occupational Safety and Health Act provides for the
protection of workers by assuring a safe and healthful work
environment. The Department of the Interior Regulations relating
to pollution control and waste disposal include leasee require-
ments against pollution of streams and surface or underground
waters. The Bureau of Land Management obligates leasees to take
reasonable precautions to prevent soil errosion, damage to
forage and timber growth, air and water pollution, damage to
fossils, historic and prehistoric artifacts. The Bureau also
requires the leasee to fill sumps and other excavations, remove
or cover debris, and to restore the surface to its original
condition at the end of field operations.

The environmental aspects of EOR require the acquisition of a considerable data base to: (1) assure compliance with state and federal laws, regulations and environmental standards, (2) to insure that a minimum of environmental disturbance occurs as a result of the EOR program, and (3) to alleviate any accidental environmental damage that might occur.

The constraints to EOR development from laws and regulations, water availability, socioeconomic impacts, environmental monitoring programs, etc., are being assessed. In addition, some areas of research have been initiated to develop specific data. These will be described briefly.

Research has been initiated to determine the rates and products of decomposition of the chemical compounds used for EOR under laboratory-simulated subsurface conditions. This work will be used to analyze the long-term viability of the large quantities of EOR compounds injected during future commercialization of EOR technology. As a companion to this work, the dispersion and chromatographic properties of the EOR compounds are also being investigated under simulated reservoir hydrological conditions. These data will be employed to predict the long-term migration properties of the injected EOR compounds.

Biological degradation rates of EOR compounds by various cultures of bacteria is also under investigation. The data will be used to determine the natural decay rate of EOR compounds which may accidentally have polluted a segment of land or a shallow aquifer. Information on the degradation kinetics of specialized cultures may be useful to actively degrade spilled EOR compounds by innoculation with specially cultured bacteria.

The transport properties and natural chemical degradation rates of EOR compounds in shallow aquifers is also being studied to develop data that can be used to anticipate the migration pattern and decay of the compounds.

Studies are also being conducted to determine the circumstances under which the injected EOR compounds will initiate local seisimic disturbances. In a related study, the reactions of the EOR chemicals with the cementing and supporting matrix of sedimentary geologic materials is under investigation. Data derived from this study will be used to determine whether long-term contact of the chemicals with sedimentary geologic materials will disaggregate the strata and cause land subsidence to occur.

Other research specific to environmental concerns of EOR is anticipated as noted in the Environmental Development Plan (2).

In the study of the environmental aspects of enhanced oi
recovery, eight areas are of concern: Atmospheric emmissions
water use, groundwater impacts, waste-water effluents, solid
wastes, occupational safety and health, physical disturbances
and noise. These are being addressed for the overall EOR pro
in a Programatic Environmental Impact Statement now being pre
pared. Each issue is also considered in individual Environme
Assessments of each field test site. Research has been initi
in areas where scientific data are not currently available to
determine possible environmental consequences of commercializ
of EOR technology.

Developments in Federal, State, and Local laws, regulati
and standards are being followed closely to ensure compliance
DOE activities and to be informed as well as to assess the pr
jected impact of the legal considerations on Enhanced Oil
Recovery.

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SESSION 7
CONTROL OF FOSSIL FUEL POWER GENERATION — CONVENTIONAL

Chairman: William Mott

Co-Chairman: Bernard Baratz

K.E. Wilzbach, C.D. Livengood, and P.S. Farber

Argonne National Laboratory

The development of new energy technologies carries with it a responsibility to identify and evaluate appropriate environmental control technologies and/or strategies. In the area of coal utilization, a continuing program for this purpose is being sponsored at Argonne National Laboratory (ANL) by the Division of Environmental Control Technology, Assistant Secretary for Environment, DOE.

As part of the program, in-depth engineering and economic assessments of available and near-term control technologies have been made by the ANL staff and several subcontractors. The topics covered include coal cleaning, NO_x control, particulates collection, flue gas desulfurization and denitrification, low-Btu gasification with combined-cycle generation, and solvent refining of coal. The development of advanced technologies, such as MHD and fuel cells, is being monitored in-house together with such other fuel cycle elements as coal transportation.

Another important aspect of the program is the comparative evaluation of different control technologies. To facilitate this effort, an extensive data base of coal properties and reserve amounts has been established. Also information to yield data from which estimates of cleanable reserves can be attempted. In order to use this large volume of data efficiently and speed the assessment task, computer models of control technologies are being developed for incorporation into a systems analysis framework representing the coal fuel cycle. To date, this framework has been used for several case studies of different power generation scenarios. These studies have included both eastern high sulfur coals and western low sulfur coals, and have utilized plant sites consistent with current practice. The comparisons have determined the least-cost mix of coal type and control technologies needed to meet current environmental regulations at each site, while at the same time producing electricity at minimum cost. Costs and energy usage for environmental control have been derived with respect to a reference 500-MW power plant. The effects of proposed regulatory changes have also been investigated and have been shown to produce significant increases in both power costs and energy usage for environmental controls.

At present, the ANL comparative assessment model is only applicable to conventional combustion techniques. As performance and economic data become available on advanced techniques such as fluidized bed combustion, MHD, liquifaction, and gasification/combined cycle systems, this information will be incorporated into the comparative assessment model. Once this incorporation has been completed it will be possible for the Department of Energy, or other interested users, to evaluate the effects of these technologies on power generation while meeting environmental regulations on a site-specific basis.

and

H. Huang, Argonne National Laboratory

This paper is a synopsis of a study conducted for Argonne National Labora
to examine the effectiveness of combustion modification methods for NO_x
applicable to coal-fired industrial boilers including low excess air, sta
combustion and burner modifications. Boiler types considered included ov
and underfed stokers, spreader stokers, pulverized and cyclone fired uni

Baseline (as-found) NO_x emissions from grate fired stokers were shown to
the range of 200 to 300 ppm. Similarly, as-found emissions from suspens
fired units were quite low as compared to comparably designed utility si
Low excess air was shown to be the most effective method on existing uni
emissions by approximately 10%. Evaluation of staged combustion and bur
fication, however, were limited due to current boiler designs. Major ha
modification/design and implementation are necessary before the potentia
techniques can be fully evaluated.

The study emphasized the numerous operational factors that are of major
to the user in selecting and implementng a combustion modification inclu
energy considerations, incremental capital and operating costs, corrosio
secondary pollutants and retrofit potentials.

THE LOW NO_X HEAVY FUEL COMBUSTOR CONCEPT PROGRAM

John R. Facey
U.S. Department of Energy
Energy Technology

and

Richard W. Niedzwiecki
NASA, Lewis Research Center

The objectives of this program are to generate and demonstrate the
technology required to develop durable gas turbine combustors for utilit
and industrial applications, which are capable of sustained, environment
acceptable operation with minimally processed petroleum residual fuels.
The program will focus on "dry" reductions of oxides of nitrogen (NO_x)
and improved combustor durability while using minimally processed petrol
residual fuels. Other technology advancements sought include: fuel
flexibility for operation with petroleum distillates, blends of petroleu

ASSESSMENT OF ENERGY AND ECONOMIC IMPACTS OF PARTICULATE CONTROL TECHNOLOGY IN COAL-FIRED POWER PLANTS

V. Ramanathan
S. Reigel
P. Gorman
P. Reider

Midwest Research Institute

Midwest Research Institute has carried out a project, under a contract with Argonne National Laboratory, to assess the economic and energy impacts of particulate control systems in coal-fired power plants. The assessment was based on major functional variables such as plant size (100 to 1,000 MWe), location, coal type, and emission standards. The work on this program resulted in the generation of algorithms, to predict equipment cost, installation costs and energy usage for various particulate control devices. The devices considered were electrostatic precipitators (hot side and cold side), fabric-filters (reverse air and shaker types) and wet scrubbers.

First, a boiler performance model was developed using variables such as plant size, coal characteristics, etc. The output from this model (i.e., flue gas flow rate, grain loading, etc.), then was utilized in control device performance models to generate required design and operating parameters for the control systems under study. These design and operating parameters were then used in the cost models.

The cost models aggregate three cost items: the first costs (capital investment), total first-year annualized costs and the integrated cost of ownership and operation of the control equipment over an assumed plant lifetime of 30 years. The models have been programmed for speedy computation. However, the algorithms are easily solvable with a hand calculator. In addition, suitable guideline values have been provided for independent variables wherever necessary. Ample case studies are presented to demonstrate use of the models.

Harvey M. Ness and Stanley J. Selle

U.S. Department of Energy
Grand Forks Energy Technology Center

Fly ashes from the combustion of many Western and Gulf Coal lignites and s
bituminous coals contain high concentrations of alkali which can be used i
wet scrubber for removal of SO_2. Additionally, dry methods of flue gas de
furization will be required for new and retrofit power installations in so
water-scarce areas in the Western U.S. The Grand Forks Energy Technology
of DOE has performed tests on utilizing fly ash in lieu of lime/limestone
130-scfm laboratory scrubber and a 5000-acfm pilot scrubber operated on a
gas slipstream at a utility burning North Dakota lignite, and on dry sorbe
and injection techniques in a 75-lb/hr pulverized coal-fired pilot combust

In this report, experimental results are presented on: 1) utilization of f
ash alkali in a wet scrubber; and 2) a series of tests designed to evaluat
trona and nahcolite as dry sorbents for SO_2 control. Ash alkali wet scrub
results include the correlation of SO_2 removal, alkali utilization, and ra
scale formation with operating conditions such as feed stoichiometric rati
(Ca/S), liquid-to-gas ratio (L/G), pH, and the concentrations of suspended
dissolved solids. Results on dry absorption of SO_2 include injection into
flue gas with subsequent collection in 1) a pilot ESP, and 2) a pilot bash
Temperatures of injection and residence times were varied to simulate full
conditions; the points of injection ranged from direct addition into the f
along with the coal, to addition at the inlet of a cold-side ESP or baghou
Data on SO_2 removal efficiency and reagent utilization are correlated with
conditions. A parallel laboratory study on the kinetics of reactions betw
the dry sorbents and flue gas SO_2 and NO_x are also described.

Meyer Steinberg, Anthony S. Albanese, and Vi-Duong Dang

Brookhaven National Laboratory

C. F. Baes, et al, Oak Ridge National Laboratory

Gregg Marland, Institute for Energy Analysis

The possible adverse global environmental effects of CO_2 buildup due to fossil fuel energy utilization have prompted an investigation of possible methods for its control. A systematic overview is presented for various routes for removal, recovery, disposal and use of CO_2 from various control points in the global system. The effect of substitute alternative non-fossil energy sources on the global CO_2 problem is evaluated. The energy and mass balances for a number of removal and recovery routes are used as evaluation criteria. Flow sheets are presented for conversion of CO_2 from various sources to synthetic carbonaceous fuels with the use of non-fossil energy. Several unique CO_2 disposal alternatives are presented and discussed.

THE IMPACT OF COGENERATION UPON EMISSIONS

Eric Lister
U. S. Department of Energy
Energy Technology

The objective of this paper is to highlight why an energy conservation technique such as cogeneration is of primary interest to a Fossil Energy group whose major criteria for success is the utilization of coal. The paper will show the following:

1) That cogeneration can reduce the emissions/useful output by a factor of 3 to 5 and is therefore one of the leading technologies for the acceptable utilization of coal and coal-derived fuels.

2) That if cogeneration on coal and coal-derived fuels is to become prominent in the industrial and commercial/ residential sectors it will require the continual development of (a) heat engines to handle the harmful agents in these fuels (b) heat recovery equipment so they can be cogenerated and (c) an on-going effort to identify and develop other critical technologies needed to make coal cogeneration the success that it promises to be.

K.E. Wilzbach, C.D. Livengood, and P.S. Farber
Argonne National Laboratory

1 INTRODUCTION

The Environmental Control-Coal Utilization Program is a continuing Argonne National Laboratory (ANL) effort sponsored since 1976 by the Division of Environmental Control Technology, ASEV/DOE. It provides in-depth evaluations of the technical, environmental, and economic aspects of control technologies for coal-based energy systems, as well as systems comparisons of alternative control technologies and/or strategies. The program was developed in response to a need within ERDA, predecessor to DOE, for independent evaluations of the capabilities of existing technology and reviews of ongoing research and development programs. In this way, the program assists the Environment staff in fulfilling its responsibility to assure the adequacy of environmental control systems for fuel extraction, conversion, and utilization.

Subjects under evaluation span the coal fuel cycle from mine mouth to waste disposal, as shown in Fig. 1, and include both current and developing

ENVIRONMENTAL CONTROLS

PRECOMBUSTION   INTEGRAL   POSTCOMBUSTION
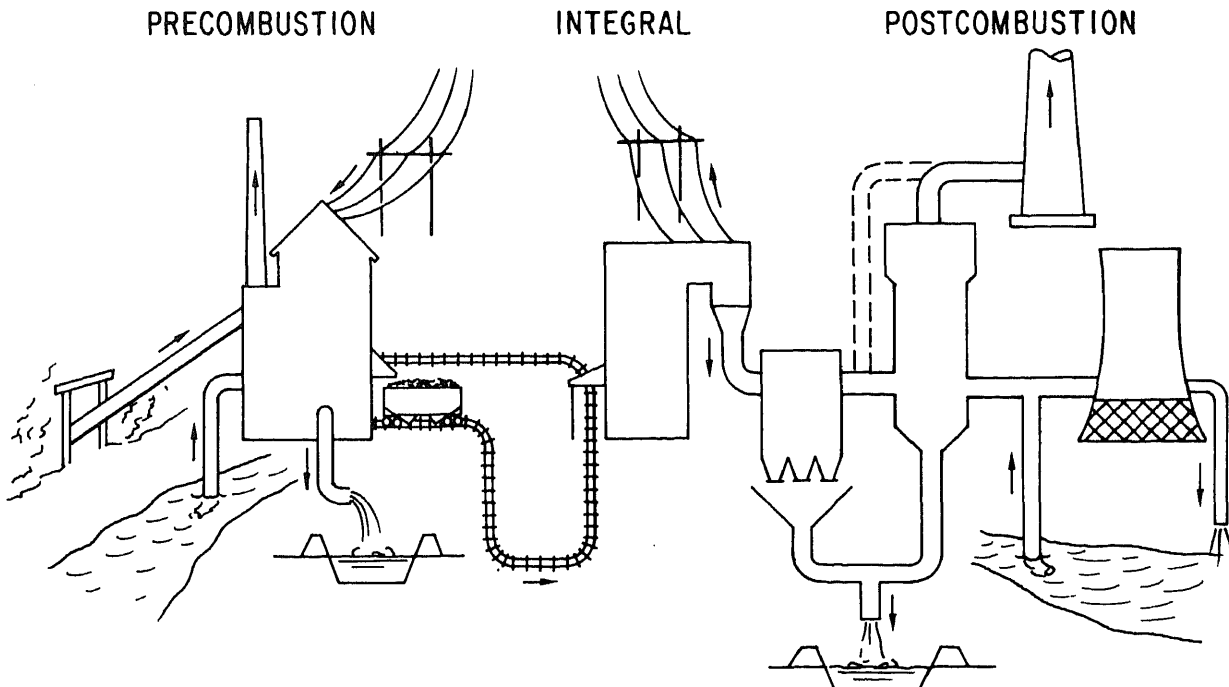
for NO_x control.
cluding flue-gas cleanup and the disposal of wastes. howeve[...]
realize that while these subdivisions are convenient, few if any o[...]
niques are truly independent of other parts of the system. The i[...]
are in fact so pervasive and far-reaching that a systems analysis [...]
demanded for a complete assessment of any of the components.

This systems perspective, coupled with the use of in-depth [...]
analyses, places the ANL program in a unique niche within the [...]
assessment efforts, being both more comprehensive than studies [...]
a single control technique or pollutant and more detailed than [...]
gional or national energy assessments. Our approach begins wit[...]
information on the costs, reliability, energy requirements, e[...]
and secondary effects of pollution control systems from reports [...]
sions with manufacturers, users, and developers of the processes[...]
effort, the capabilities of the in-house staff are supplemented b[...]
able use of subcontractors and consultants with special capab[...]
expertise. Evaluation of this information leads to the identi[...]
problem areas, inherent process limitations, and high-payoff are[...]
search and development.

Further, the information on individual processes is part o[...]
to technology comparisons that use a computerized systems-ana[...]
odology. These comparisons are used to identify the potential role[...]
technologies as a function of environmental regulations, location[...]
of development. In cases where several approaches appear to be c[...]
it is often possible to identify critical process parameters th[...]
most effective in altering the existing balance or that are s[...]
small changes in environmental requirements.

The initial studies performed in the program were devote[...]
to surveying available technologies/strategies for the cont[...]
pollutants (SO_2, NO_x, and particulates) from coal-fired utili[...]
These were presented in our first report, ANL/ECT-1, together w[...]
of existing federal and state environmental regulations and the [...]
fects of pollutants. Some attention was also given to the contr[...]
pollution, disposal of solid wastes, and the status of fluidiz[...]
bustion (FBC) technology. Information gathered in that firs[...]
studies has subsequently been used to identify and scope mor[...]
assessments performed by subcontractors to ANL, resulting in a[...]
series of reports dealing with individual control technolgies. [...]
with these studies, the ANL staff has been analyzing areas o[...]
technology not previously covered and has begun to study advance[...]
under development. All of these assessments are briefly revi[...]
following section. The third part of the paper presents the r[...]
typical technology comparison based on alternative regulatory [...]

The technology assessments performed to date have focused on
able and near-term technologies in order to establish an informatio
suitable for technology comparisons and for the evaluation of deve
environmental regulations that may affect coal-based energy systems.
data will also serve as benchmarks in analyses of mid-term technol
Several such studies are now being developed by the program staff an
be noted in the following discussion.

2.1 PRECOMBUSTION CONTROLS

Precombustion, as defined in this program, encompasses all oper
from the mine mouth up to the fuel utilization step (the boiler, in c
tional systems). It can range from a simple conveyor belt and storag
in the case of a mine-mouth plant to complex arrangements involving s
stages of transportation and storage coupled with coal conversion
alternative form.

2.1.1 Coal Transportation

Transportation facilities (rail, barge, truck, pipeline) are
significant in determining both the availability and delivered co
specific coals or coal products. Thus, the fuel choice at a particula
and, through the fuel characteristics, the selection of environmenta
trols can be influenced by the transportation system. There may als
significant consumption of fuel or other resources and production of
tants during transport, although the latter are admittedly widely distri
However, these transport-related pollutants will become more noticea
the system evaluation as on-site emissions are lowered.

An extensive survey of the available literature on coal transpor
has been made by the program staff with particular emphasis on environ
effects and costs. This information will be incorporated into future co
tive systems evaluations.

2.1.2 Coal Preparation and Cleaning

By far the most extensive effort in the precombustion area ha
an assessment, performed by Bechtel Corporation, of coal preparati
cleaning technology. That study addressed current industry practic
developing methods for both physical and chemical cleaning, as well
effects of cleaning on important coal properties. Detailed flow sheet
used to generate estimates of costs and environmental impacts due to cl
specific coals. Although the results were far too comprehensive to sum
here, one can conclude that significant sulfur reductions are possib
carefully selected coals if fine-coal cleaning is employed. However
technique carries with it potential environmental problems in the dewat
handling, and transportation of coal fines. Also, significant cos

ANL to determine the cleanability of U.S. coal reserves. Using da
from the U.S. Bureau of Mines, about 18% of this country's dem
reserves were matched with washability data and merged into a singl
data file. This included 35% of the reserves that account for 80%
production.

2.1.3 Solvent Refined Coal (SRC)

More extensive coal processing is represented by the SRC-1 (
duct) and SRC-2 (liquid product) technologies. A preliminary sur
literature and pilot plant results for SRC-1 was performed for our
Air Products and Chemicals, Inc. That project also included deve
product costs and material and energy balances for a 20,000-tons-pe
feed plant. Product costs were estimated at about $3.25/10^6$ Btu (1
for a delivered coal costing $25 per dry ton. Finally, the pro
SRC-1 as a fuel were discussed relative to conventional pulverized
need for some burner redesign was identified, as was a potential pr
high NO_x emissions.

A more recent study conducted by the ANL staff surveyed env
monitoring results obtained at the Ft. Lewis pilot plant. No p
meeting existing air and water standards were identified, but the
of the plant and the limited testing data available preclude any fi
sions at this time.

2.1.4 Coal-Oil Mixtures (COM)

The use of COM has been widely discussed as a potential fuel
ing boilers. It would further the nation's goal of greater coal u
while, it is hoped, creating minimal environmental problems.
study of this technique by the program staff has revealed high
degrees of success in producing, storing, transporting, and firing
ways in which different oil and coal properties affect the COM sta
the consequences of prolonged use are not well-defined.

Some add-on flue-gas cleanup controls will probably be re
COM use, but the requirements will vary with the sulfur contents o
and oil used, as well as their relative proportions. This is due t
that the applicable regulations are generally a combination (on a w
cent basis) of those for coal and oil taken separately.

2.2 INTEGRAL CONTROLS

Taking advantage of inherent system characteristics to ach
ronmental control goals is obviously attractive insofar as it redu

looked.

2.2.1 Combustion Modifications for NO_x Control

An analysis of combustion modification techniques for NO_x co
utility boilers was performed by KVB, Inc. It identified staged co
and low-excess-air operation as the most cost-effective methods for
units. For new units or extensive retrofits, improved burner desi
found to offer promise of even greater reductions. There is cons
variation in the NO_x-reduction potential between various combinat
boiler type and combustion modification, but the reductions now att
commercial units are generally less than 50% and typically only 20-30%
ational concerns are centered mainly on unresolved questions about c
arising under these operating conditions.

KVB is presently developing an update of this report to includ
opments in the field during the past year. Also, they have recen
pared a similar study of NO_x control through combustion modificat
industrial boilers. Similar techniques are used, but the analysis is
cated by the wide variation in furnace types and sizes. This work
tiated in anticipation of increased policy interest and regulatory
related to the industrial use of coal.

2.2.2 Fluidized-Bed Combustion (FBC)

The possibilities inherent in FBC for integral control of SO_2
while providing economic power for utilities and industry have bee
discussed. The strong base of information that exists at ANL for th
nology has enabled the program staff to develop assessments of FBC c
ties and existing or potential problems. One such study is now in
tion.

However, in order to obtain an independent point of view, Mit
oration has been engaged to analyze results reported at the 5th
tional Conference on FBC held in December 1977. They have had e
access to these data as conference organizers. The method used ap
be unique in the way data, issues, problems, and information gaps
sented in matrix form. Also, it uses a linear approach to conclusio
opment that is independent of prior knowledge regarding issues or p
This may be regarded as either a strength or weakness, depending up
needs. This work is now nearing completion.

Foster Wheeler Corporation anliminary assessment of six systems based on moving-bed (Lurgi), f
(IGT), and entrained-flow (Foster Wheeler) gasifiers processing
and Montana coals. With this work as a basis, a more extensive ev
has been undertaken by United Technologies Research Center. In add
the above gasifiers, a Texaco unit is being included in this study.
both Illinois bituminous and low-sulfur Montana subbituminous coals h
used in the analyses. This work is now nearing completion.

Both studies have found the G/CC systems to emit lower quant
pollutants than conventional power plants and to be economically com
with existing technologies. However, the wide band of uncertainty
associated with these cost estimates precludes any firm conclusions
time. This uncertainty is largely due to the need for further e
development of both gasifiers and the advanced high-temperature gas
required. These developments will be crucial to commercialization
technology, since significant cost advantages must be shown before
novel approach will be accepted by the utility industry.

2.2.4 Other Developing Technologies

Assessments of two additional coal utilization technologies
porating integral controls are now being planned. Advanced molten-c
fuel cells may offer unique siting opportunities as well as highly e
coal utilization. The cells are generally viewed as environmentally
but the environmental control aspects of the fuel conversion process
relationship to the fuel cells merits analysis.

Power plants based on magnetohydrodynamics (MHD) also of
promise of high efficiency. An upcoming study will explore nume
answered questions regarding the efficiency of both integral and
environmental controls for this technology.

2.3 POSTCOMBUSTION CONTROLS

Most questions about environmental controls have been centere
costs and effectiveness of postcombustion cleanup systems. For that
a very significant part of our program's effort has been devoted
area.

2.3.1 Particulate Collection

Several studies have been devoted to the assessment and mod
particulate collection systems. The first of these, conducted by
Research Institute, discussed the sources and characteristics of
applicable emission regulations, available technologies, technique

between hot and cold ESPs and baghouse fabric filters was found t
on a combination of emission regulation, coal sulfur and ash contents,
characteristics.

In order to further explore the tradeoffs between different
Midwest Research Institute was engaged to develop energy and economi
of available particulate collection equipment suitable for our com
evaluations. That model supplements a previously developed computer
written at ANL (see Sec. 3.1).

Another study was performed at Manhattan College with the
assessing collection techniques for fine (submicron) particulate
Particles in this range are of great concern, because they are respir
may carry toxic trace elements. Topics addressed in the study incl
formation and characterization of fly ash for different coal and boile
the performance of both conventional and novel devices, and energy, e
and operational aspects of the alternatives. Baghouses were ident
the most attractive option among available alternatives as emission s
are tightened, although ESPs may be competitive for high-temperatur
pressure applications. Novel devices under development were judged
little promise for improvement in fine-particulates control before
best.

At the present time, we are sponsoring a study by KVB, Inc. t
tigate any correlations between combustion conditions and particulat
tion. If sufficient data are found to be available, this study wil
in a better understanding of how particulate control is influenced
and combustor characteristics.

2.3.2 Flue Gas Desulfurization (FGD)

No other area under the purview of this program has been the
of such controversy as FGD. This is due to a number of factors, f
strong regulatory pressure for development, a limited base of exper
utility applications, and the lack of firmly established "standard"
or design procedures that consistently produce satisfactory perf

A study surveying the status of FGD, worldwide as well as
U.S., was performed for us by the Tennessee Valley Authority (TVA)
than 20 different process types were identified. These were divide
equally between those yielding throwaway and recoverable products.
the only significant experience in this country is for throwaway
limestone (L/LS) systems, which comprise about 95% of the operati
systems on a megawatts-served basis. The study identified numero
ational problems and high maintenance requirements for these sys
pointed out that there is as yet very little experience with FGD
fired with high-sulfur coal.

Subsequent projects by both TVA and Batelle Columbus Labo
have sought to utilize the available data to model performance and

2.3.3 Flue Gas Denitrification

If regulatory requirements for NO_x reduction in stationary
are increased, the combustion modification techniques noted in Sec. 2
no longer be adequate. In anticipation of such a possibility, we r
KVB, Inc. to include in the NO_x-control study mentioned previously
tion on gas-phase reduction of NO_x. Ammonia injection appears pr
but large-scale coal-fired tests are needed to verify its effective
investigate costs and secondary pollutants.

In another assessment, TVA reviewed processes currently bein
oped for the simultaneous removal of NO_x and SO_2 from flue gases.
such processes, most Japanese in origin, were evaluated in some deta
most advanced types were found to be dry selective catalytic reduc
wet oxidation-absorption-reduction. However, further process deve
scale-up, and application to flue gas from coal-fired boilers are
before realistic assessments of their potential roles in the U.S.
made.

2.3.4 Solid-Waste Disposal/Utilization

The question of solid-waste disposal has been reviewed by
ANL staff and several subcontractors in connection with studies of
late control, FGD, and FBC. In general, the concerns identified
volved about cost, questions of land-use policy, and the possibili
water pollution through leaching. Passage of the Resource Conserva
Recovery Act (RCRA) has greatly increased concern regarding the
question because vastly increased disposal costs could be in the offi
view of this area is planned pending an evaluation of the regulatio
formulated by the EPA.

2.3.5 Waste-Heat Disposal/Utilization

The disposal/utilization of power plant waste heat is rightfu
sidered as an environmental control technology, and one that has
been the subject of considerable controversy. Assessments of the env
tal, performance, and economic factors associated with the various
techniques are now being planned to supplement preliminary data gat
the ANL staff.

The comparative assessments draw upon information generated
detailed technology evaluations. These comparisons can involve the
coal-to-power system, or they may focus on specific system elements,
particulate control. In order to provide this flexibility, a
approach is used wherein each module represents a significant, and
nically separable, component of the system. The modules are gradual
computerized as sufficient data become available through the acquisi
development of models. Several computerized data bases are also in
ment as sources of input information for the comparisons.

3.1 MODELS AND DATA BASES

One data base was the result of the effort described previo
integrate coal reserve and washability data. At this time, integrat
been achieved for 189 different state/county/bed combinations. Howev
fact that many coals were tested more than once leads to a total of a
integrated data sets. Present plans call for significantly expandi
sample using additional washability information collected recently.

A related data base has been developed using the Bureau of Min
serve and analytical data tapes. More than 56,000 separate entries
available in the base. The information is useful in providing re
coal analyses for the evaluation of control performance, identifying
differences in coal characteristics, and assessing coal variability.

Modeling efforts by subcontractors to the program have been de
in the preceding sections. These efforts have included the entire
generation system, FGD, and particulate control. The ANL staff h
been active in this area with the development of a particulate contro
incorporating cost and performance information for ESPs, baghous
scrubbers. The model calculates energy consumption, capital cost,
cremental electricity cost for each option as a function of coal prop
plant size, and regulatory constraint. An example of the program ou
shown in Fig. 2 for a comparison involving a slightly cleaned, low-
eastern coal. Note that the most economic options in this case are
ESP and the baghouse, with the hot ESP favored under present NSPS (0.
Btu) and the baghouse having a slight advantage under the proposed
NSPS (0.03 $lb/10^6$ Btu). This type of analysis was used to sel
least-cost option for each regulatory alternative in the followi
parison.

3.2 EXAMPLE COMPARISON

Recent months have seen a vigorous debate waged over the
revisions to the federal New Source Performance Standards. For this
we have developed a comparison of two plausible regulatory scena
applied to the reference case described in Table 1. The environment
trols specified in Table 2 were added as needed, and adjustments
size were made to maintain the output at 500 MWe.

WEST VIRGINIA LEVEL 2

COLD ESP - SOLID CURVE
HOT ESP - DOTTED CURVE
BAGHOUSE - DASHED CURVE
SCRUBBER - DOT/CHAIN CUR

ANNUALIZED COST OF POWER (MILLS/KWHR)

PARTICULATE EMISSION REGULATION (LB/MILLION BTU)
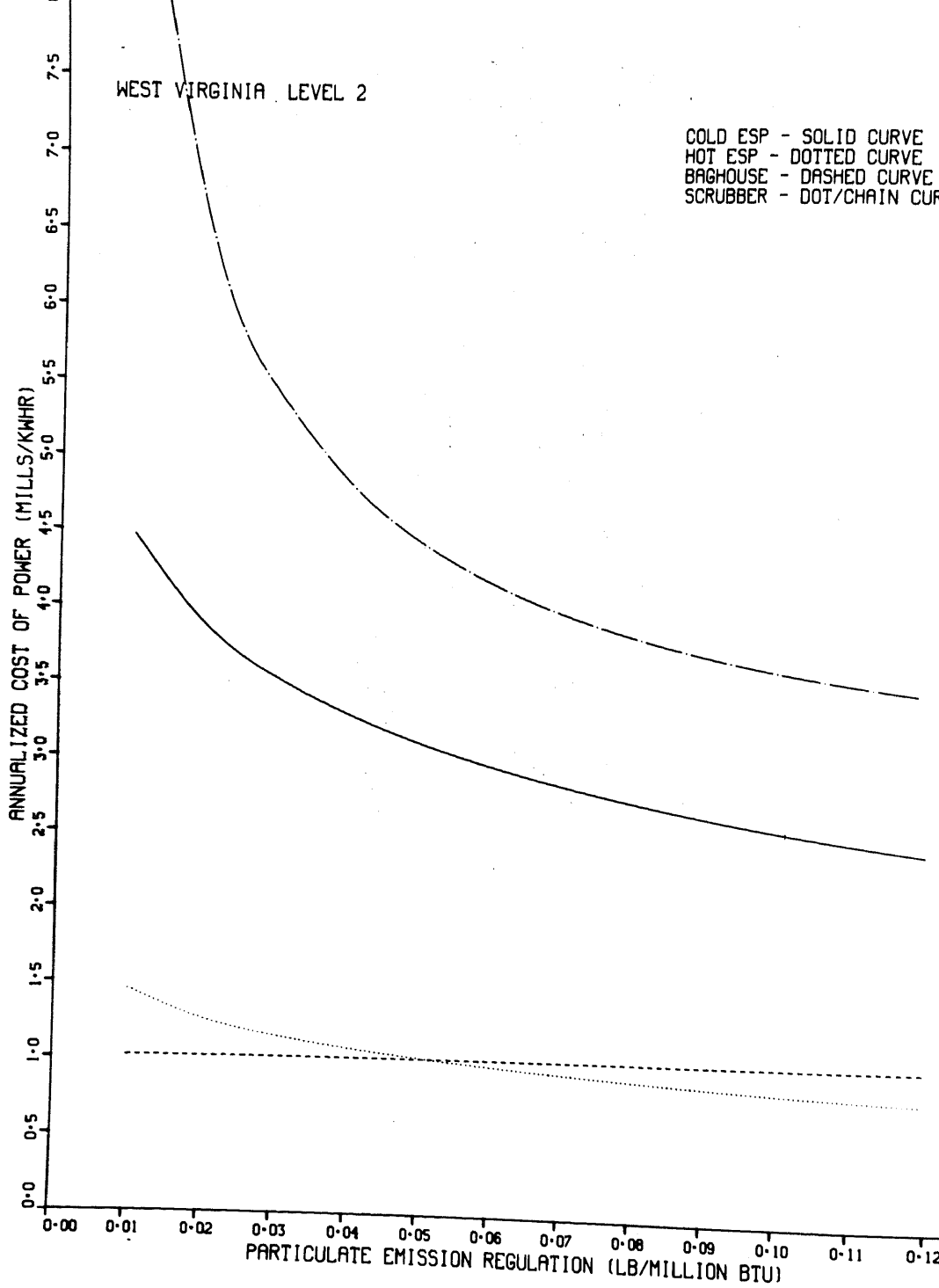
Fig. 2. Cost/Performance Tradeoffs from
ANL Particulate Collection Model

Location	Northern Illinois
Net output	500 MWe
Type	Conventional pulverized-coal fired
Heat rate	9200 Btu/kWh
Environmental controls	None
Coal characteristics (as received)	10,500 Btu/lb, 16% ash, 0.6, 1.0, 3.0, or 5.0% sulfur

Table 2. Environmental Controls

Particulates	Lowest cost option chosen from hot or cold ESP and baghouses.
SO_2	Limestone slurry FGD with combined fly ash and sludge disposal in a clay-lined pond.
NO_x	Combustion modifications.
Cooling	Wet mechanical draft cooling towers instead of the reference-case once-through cooling.
Water Treatment	System corresponding to the best available technology.

The object of this comparison is to illustrate the costs corres to different levels of environmental control. These costs are ass with certain benefits to society, foremost of which are the 500 MW o tricity produced by the plant. However, while a cost-benefit anal conceptually appealing for arriving at the optimum control level, it vented at this time by uncertainties in pollutant-damage estimates lack of a consensus on the costs of health effects. Therefore, we wi sent the costs separately in terms of economic penalties applied to t of power, residual pollutant emissions, and the consumption of res

Air pollution regulations used for this example are shown in T Two different sulfur control levels were used, since this is the greatest sensitivity for costs and performance. These alternatives pond to the full scrubbing requirement recommended by the EPA, with removal determined on the basis of either daily or monthly averages. four different coal sulfur levels were used, as shown in Table 1 (al coal properties were either held constant or adjusted to keep key par like flue-gas volume, constant). At 0.6% sulfur, the coal could achi

Present NSPS:	
NO_x	0.7 lb/10^6 Btu
Particulates	0.1 lb/10^6 Btu
SO_2	1.2 lb/10^6 Btu
Alternative NSPS:	
NO_x	0.6 lb/10^6 Btu
Particulates	0.03 lb/10^6 Btu
SO_2	85% removal or 92% removal, both with a maximum level of 1.2 lb/10^6 Btu and a minimum required level of 0.2 lb/10^6 Btu

pliance with the present NSPS with no additional controls, while at
fur some flue-gas bypass could still be used to eliminate reheat
ments. Both of these low sulfur coals require full scrubbing unde
ternative standards. The 3% sulfur level is representative of coal
many utilities and requires FGD in all cases. At 5% sulfur, the r
"ceiling" comes into play since greater than 85% removal is required
a level of 1.2 lb/10^6 Btu. Thus, these four sets of coal properti
yield a representative spectrum of SO_2 control costs under all of th
considered.

Based on the foregoing assumptions, the incremental electric
(in 1980 $) and pollutant burdens associated with the environmental
are presented in Figs. 3 and 4. Note that they are expressed as eit
or lb/MWh in order to more directly relate costs and benefits. A
format illustrates how, when regulations are based on energy inp
lb/10^6 Btu), the addition of energy-intensive environmental cont
one pollutant can actually increase emissions for others. For inst
spection of Fig. 3 shows that the addition of scrubbing for SO_2 as
of increasing coal sulfur (under present NSPS) serves to increase th
of NO_x and particulates emitted, since the plant heat rate changes f
9500 to nearly 10,000 Btu/kWh. This effect on performance is a
dramatically in Fig. 5, where the energy consumption due to controls
For low sulfur coals, the energy requirements for pollution contro
are more than doubled under the proposed changes.

The incremental economic costs shown in Fig. 3 are due primari
increasing FGD requirements that result in both additional equipm
and large increases in the amount of solid waste requiring disposal
in Fig. 4). It is clear from the figures that there is a tradeof
electricity cost and pollutant emissions and that the change in for
SO_2 regulation also changes the form of the cost balance. Under
sent NSPS, emissions are fairly uniform across all coal types, and,
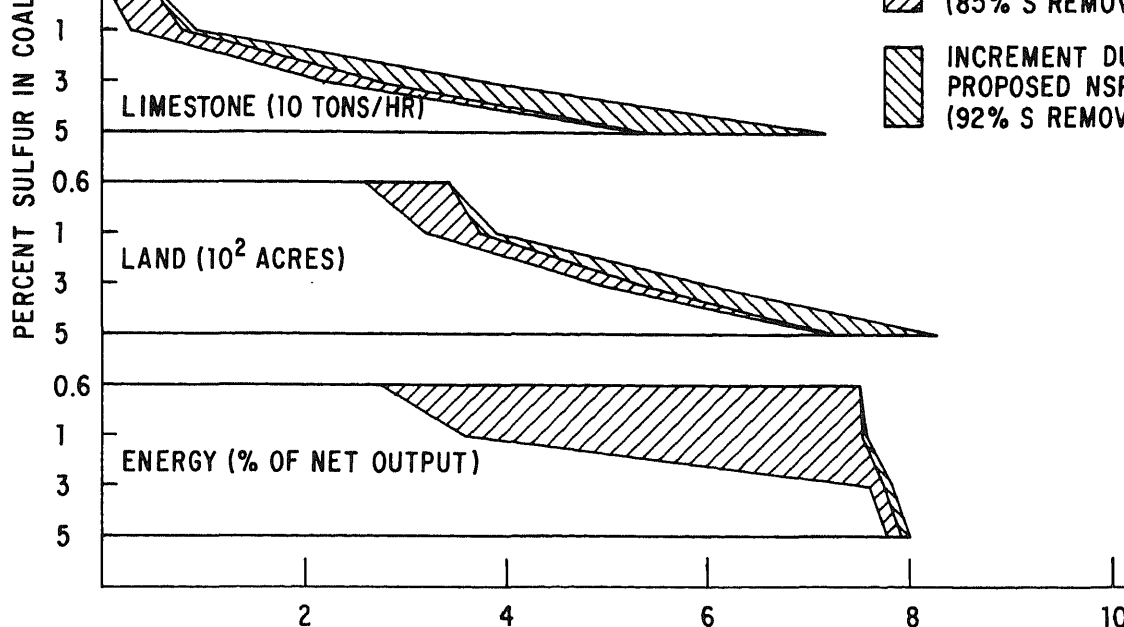
Fig. 5. Resource Consumption by
Environmental Controls

delivered prices, the economics favor the use of low sulfur coal.
other hand, a fixed percentage-reduction requirement for SO_2, coupled
very low "floor," greatly reduces the cost differential while producing
variations in emissions. This acts to favor the use of local coals i
areas of the country. However, where that implies a shift from low- t
sulfur coal use, air emissions will not be significantly reduced and
wastes will increase by a factor of 2-4.

Resource requirements, as shown in Fig. 5, also increase.
requirements are dominated by condenser cooling, so that the increase
the addition of FGD is less dramatic than one might anticipate. H
this is a very site-specific item, and the choice of a less humid l
would result in increased water losses because of waste-pond evapo
The sludge pond is also responsible for the increases in land require
These closely follow the changes in solid-waste burden, since a consta
depth of about 20 ft was used in the calculations. Note that the cha
land-use impacts due to FGD are somewhat damped by the existing nee
ash disposal.
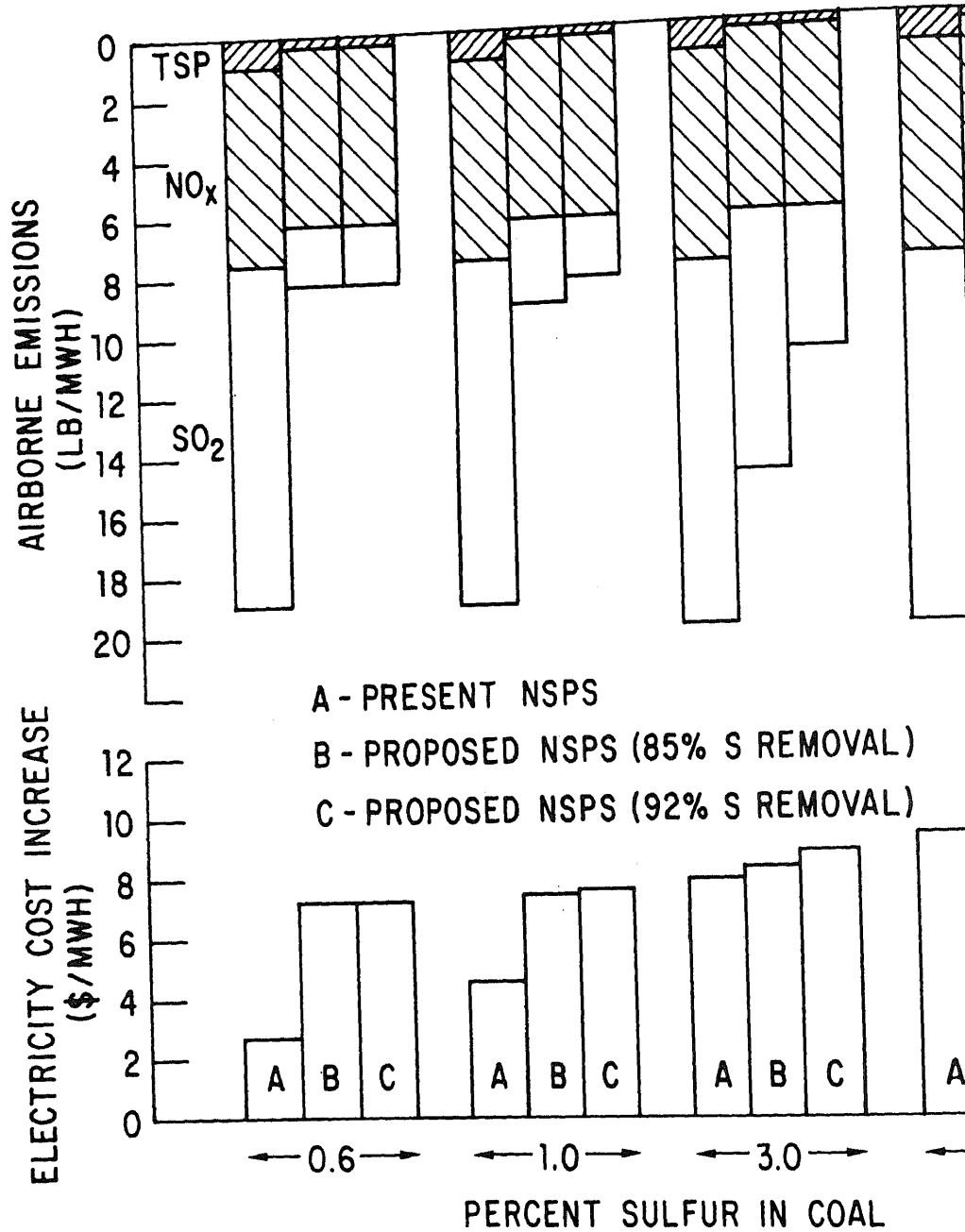
Fig. 3. Environmental Control Costs
and Residual Air Emissions
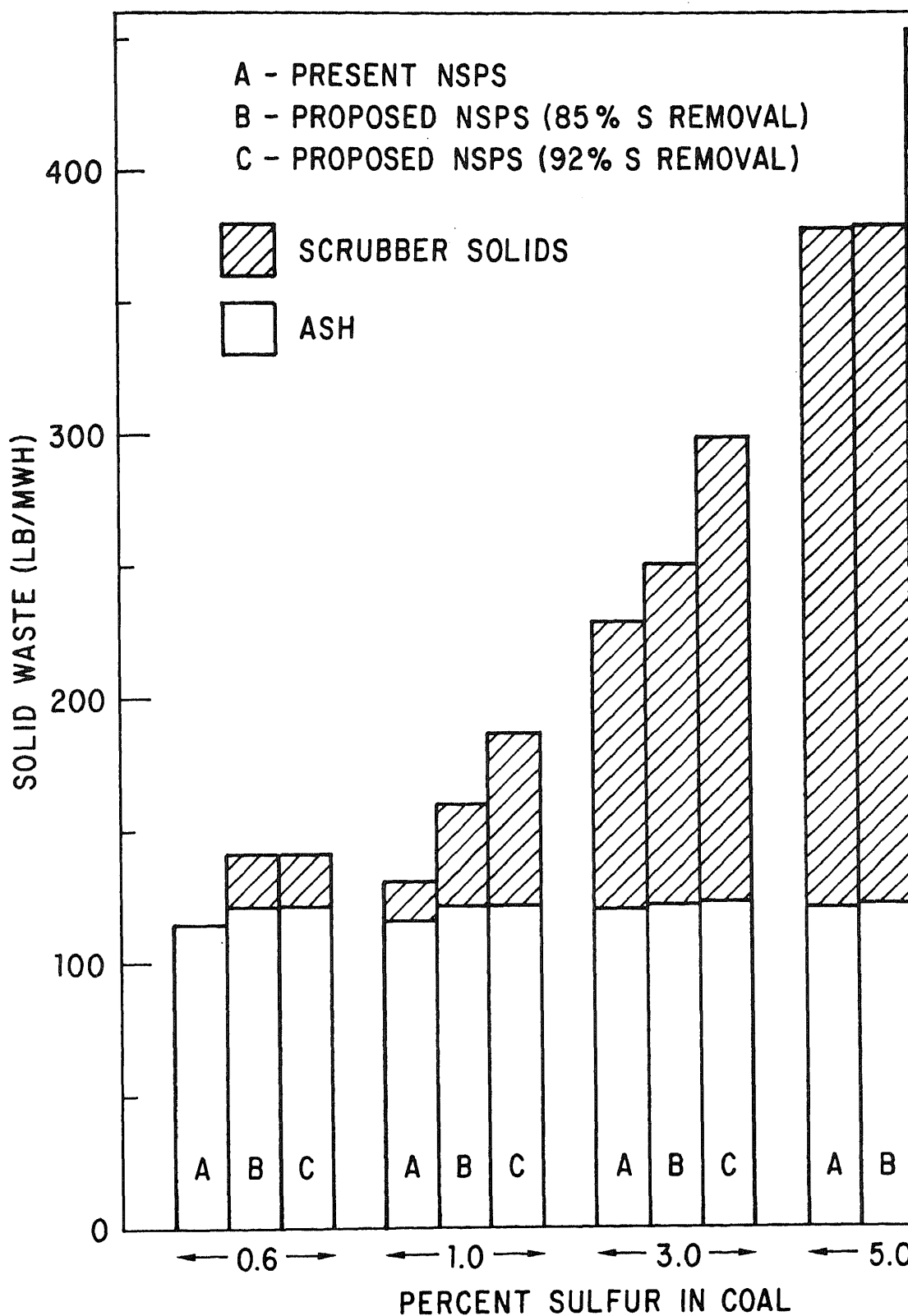
Fig. 4. Solid Wastes from

large, such increases should not be dismissed out of hand, since [...]
human and environmental costs will be incurred in mining and transp[...]

4 CONCLUSIONS

The preceding example has provided ample indications of [...]
environmental controls affect other parts of the energy system and a[...]
(air, land, and water). If precombustion controls had been analyz[...]
more far-reaching interactions would have been seen. Thus, it is e[...]
that a systems perspective be adopted and faithfully followed in ev[...]
the performance of controls, the desirability of regulatory changes[...]
environmental aspects of research and development programs.

The many tradeoffs between costs and benefits also argue pers[...]
for basing emission restrictions on energy output rather than inpu[...]
would not only provide a more direct measure of the cost/benefit ra[...]
would promote the use of efficient controls and conserve resources [...]
viding an additional incentive for efficient plant operation. Furt[...]
it could greatly enhance the attractiveness of measures to utiliz[...]
energy, as in cogeneration. Figure 6 illustrates for particulates [...]
that emissions are presently a function of heat rate (plant efficie[...]
shown by the upper and lower lines. The middle line shows how a re[...]
based on output energy ties emissions to the system benefit and w[...]
effect, penalize less efficient plants by requiring greater red[...]

Lastly, our assessments and comparisons indicate that there [...]
clear-cut choices and no panaceas in environmental controls for c[...]
None of the developing technologies has such an economic advantage [...]
realities of cost escalation and market competition could not possib[...]
it to negligible proportions. In that case, experience has shown [...]
dustry will opt for what is known best -- existing technology. [...]
ticular, utility companies are quite conservative and intrinsic[...]
luctant to accept new technologies with uncertainties in commercial[...]
mance and costs. This is not meant to imply that development [...]
systems should not be undertaken, but only that the performance [...]
potential of each approach must be scrutinized with great care and re[...]
each stage in its development. Changing priorities, policies, and [...]
tions have the power to shift the cost/benefit balance far more quic[...]
any but the most unusual technological developments.
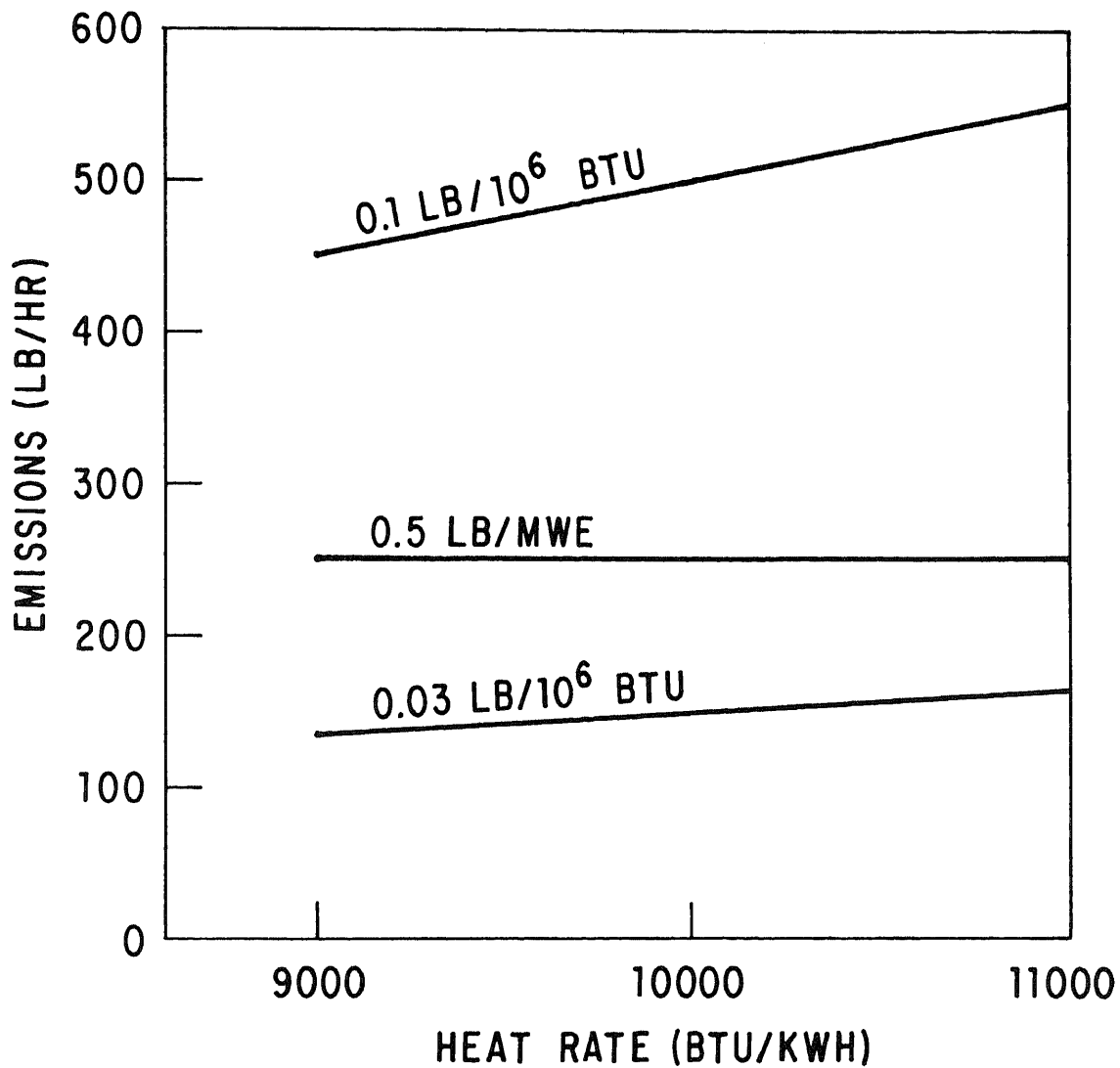
Fig. 6. The Effects of Alternative Regulatory
Strategies on Emissions

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1. INTRODUCTION

Emissions from stationary combustion sources have been effectively co
to 10% or less of their initial levels for all major or criteria poll
except NOx. The conversion of fuel-bound nitrogen to NO during the c
tion process makes the control of NOx emissions from coal-fired boile
particularly difficult. However, coal is our largest natural fossil
source and DOE is responsible for developing methods of utilizing coa
environmentally acceptable manner. Coal is used extensively for powe
ration by the electrical utility industry but the increased use of co
industrial applications cannot be ignored, particularly in air qualit
trol regions where NOx air quality standards are barely being met or
Consistent with their responsibilities, EPA has established research
NOx emissions from coal combustion of 200 ppm by 1980 and 100 ppm by
is also currently assembling background technical support documentati
yet-to-be proposed industrial boiler NOx emissions regulation.

For the reasons outlined above, a need existed to conduct a comprehe
state-of-the-art review of all potential combustion modification meth
NOx control on coal-fired industrial boilers. Combustion modificatio
the past been the most cost-effective approach to limiting NOx forma
emissions. With the resurgence of interest in spreader stoker units
desirable to document the most recent technical developments plus lo
R&D needs associated with that boiler design category.

2. NOx EMISSIONS FROM COAL-FIRED INDUSTRIAL BOILERS

NOx is formed during coal combustion from two sources: (1) the therm
fixation of atmospheric oxygen and nitrogen, and (2) the conversion o
bound nitrogen. The availability of oxygen, as well as temperatures

local stoichiometry, temperature, mixing and residence time at these con-
ditions. Burner, grate and furnace configurations are important factors i
NOx formation since they influence mixing patterns, heat release and absor
tion rates as well as residence times within the furnace.

Significant variations in firing methods and combustion conditions occur
in industrial sized coal-fired boilers. The smaller units (up to approxi-
mately 250,000 lb/hr steam flow) are largely stoker-fired units. They
differ primarily in the mechanical method of coal introduction into the
furnace, including overfed, underfed and spreader stokers. These units ar
characterized by release and combustion of volatile materials above the gr
and bed combustion of the resulting char on the grate. In spreader stoker
the coal is hurled into the furnace so that devolatilization and some part
combustion occurs prior to landing on the grate. In all stokers, the bulk
of the combustion air is supplied through the grate.

Larger boilers generally use suspension firing in pulverized or cyclone
units. In these units the combustion air is supplied with the coal throug
individual burners. Several configurations of pulverized-fired units are
These include tangential, single wall, horizontally opposed and verticall
fired boilers. They differ primarily in the location, arrangement and typ
of burners in the furnace. Other than size and the corresponding number o
burners, these boilers are similar in design to utility sized units.

3.   DEPENDENCE OF NOx EMISSIONS ON BOILER TYPE

NOx emissions from industrial boilers are dependent on the boiler design
primarily because variations in the type of combustion influence the con-
version of fuel nitrogen. A summary of baseline (or as-found) emissions
levels by boiler firing type is presented in Table 1.

Table 1. Summary of Baseline NOx Emission Levels

Firing Type	NOx Emissions, ppm ($3\% O_2$, Dry)
Suspension Fired	
Cyclone	800
Single Wall	350-900
Horizontally Opposed	500
Tangential	400-500
Vertical	---
Stoker	
Underfed	250-350
Overfed	200-300
Spreader	300-600

small, comparably fired utility boilers (Ref. 1). ... [...] of
industrial boiler NOx emissions on boiler size or capacity is very wea[k]
unlike many coal-fired utility boilers. Typical baseline NOx emission[s]
boiler capacity for different types of industrial boilers are shown in [...]
1 for comparison purposes.

Although industrial boiler NOx emission rates are generally lower than [...]
utility boilers, considering the stoker emission levels, the total ann[ual]
emissions from the industrial category are significant and cannot be i[gnored]
in meeting air quality standards. An appreciation for the industrial [...]
coal use and annual NOx emissions by boiler type can be gained from Ta[ble ...]
It should be noted that stoker units represent approximately 80% of to[tal in-]
dustrial boiler NOx emissions, in spite of their low emission levels, [because]
of their large population and fuel use.

Table 2. Estimates of Coal Use and NOx Emissions*
From Industrial Watertube Boilers for 1972

	Coal Usage		NOx Emission[s]	
Pulverized Fired	10^{12} Btu/Yr	%	10^3 TPy	%
Tangential	80.0	4.8	30	6.[...]
Horizontally Opposed	28.8	1.7	12	2.[4]
Single Wall	52.8	3.2	21	4.[...]
Vertical	5.3	0.3	2	0.[4]
Cyclone	35.0	2.1	28	5.[...]
(Subtotal)	(201.9)	(12.1)	(93)	(18.[9])
Stoker Fired				
Spreader	641.2	38.3	179	36.[...]
Underfed	567.7	34.0	144	29.[...]
Overfed	169.6	10.1	53	10.[...]
Not Classified	91.2	5.5	25	5.[...]
(Subtotal)	(1469.7)	(87.9)	(401)	(81.[...])
Total	1671.6		494	

*Ref. 2

4. COMBUSTION MODIFICATIONS TO REDUCE NOx EMISSIONS

Combustion modifications including low excess air and staged combustio[n ...]
been effectively used to reduce baseline NOx emissions concentrations. [...]

NOx, ppm (3% O$_2$, DRY)

900
800
700
600
500
400
300
200

0   100   200   300

KLB STEAM/HR

Cyclone

Pulverized

Spreader Stoker

Underfed Stoker

Overfed Stoker
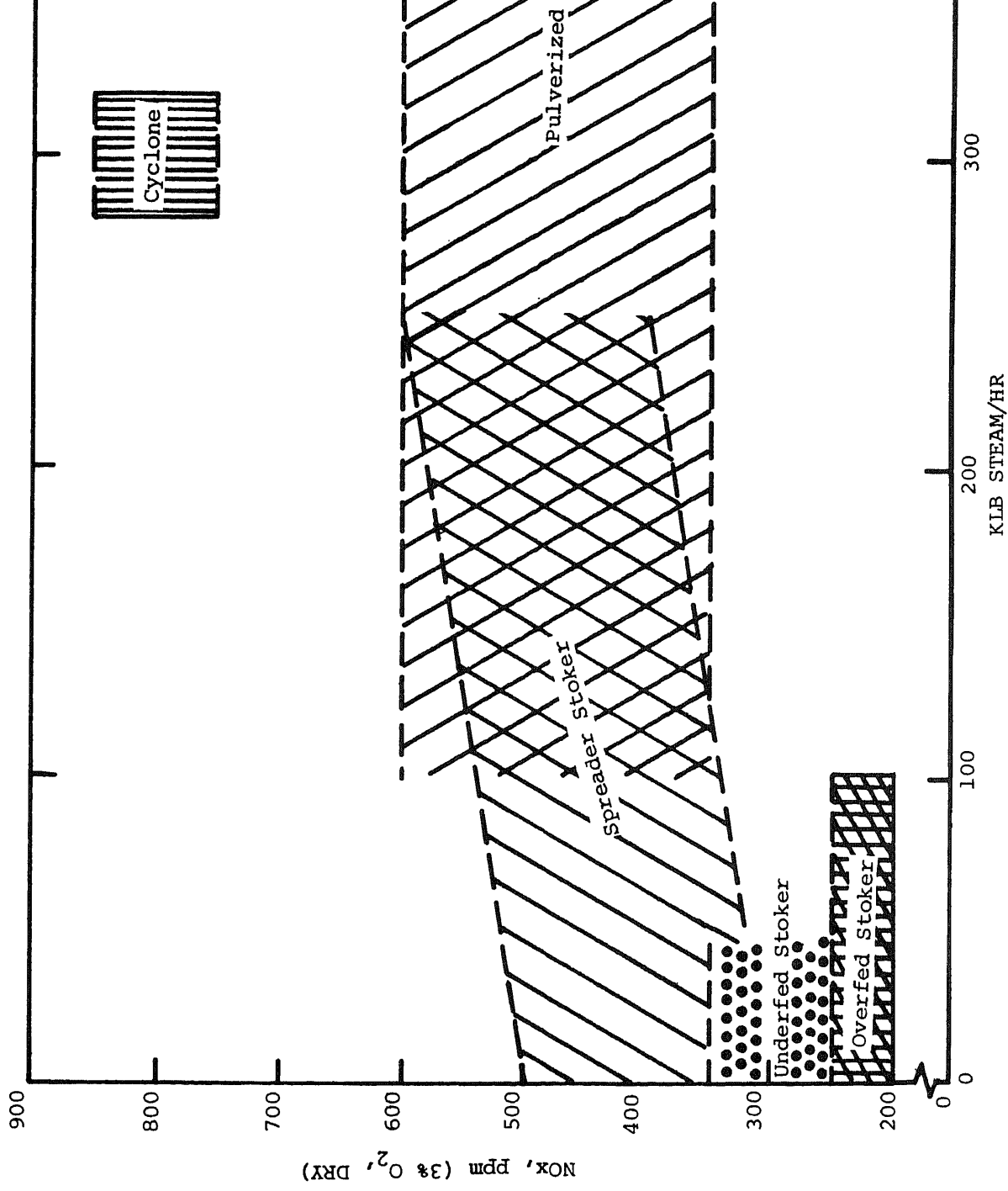
Table 3. Summary of NOx Reduction Potential

Firing Type	LEA	Air Register Adjustment	BOOS	Simulated OF Injection Systems	Au Burn
Suspension Firing					
Cyclone	5%	-	-	-	-
Single Wall	5 to 10%	15%	30 to 45%		
Tangential	10%	-	40%	-	-
Stokers					
Underfed	10%	NA	NA	-	
Overfed	10%	NA	NA	0 to 20%	-
Spreader	10 to 15%	NA	NA	0 to 5%	10 t

NA - Not applicable

Low excess air (LEA) involves operating the boiler with a reduced amo of overall excess air. Minimum excess air levels are determined by u factory boiler operating conditions with excessive carbon carryover.

Industrial boilers tend to be operated at various levels (0 to 5% O_2) above practical smoke limits due to improper air or fuel distribution, ment limitations, operator/maintenance neglect, etc. The reduction p presented in Table 3 apply to a one-percent reduction in excess O_2 le In many instances, the actual reduction potential of LEA (considering larger available margin in excess O_2) was greater than the more comple techniques. For spreader stoker units, a reduction in excess air can a significant reduction in NOx as shown in Figure 2. In fact, LEA is the most effective NOx control method on existing stoker units.

Staging the combustion process into primary and secondary combustion regions can be achieved through burner-out-of-service (BOOS) and overf air (OFA) operation. These techniques are very effective in reducing emissions by reducing the availability of oxygen in the primary combus zones. The application and reduction potential of these techniques ar highly dependent on the location and flexibility of the unit's coal ar supply to the furnace.

BOOS is implemented on pulverized coal-fired units by terminating the flow of coal to selected burners (and thereby increasing coal flow to t maining burners) while maintaining air flow through all burners. In th ner, sufficient segregation of fuel-rich and air-rich zones are created
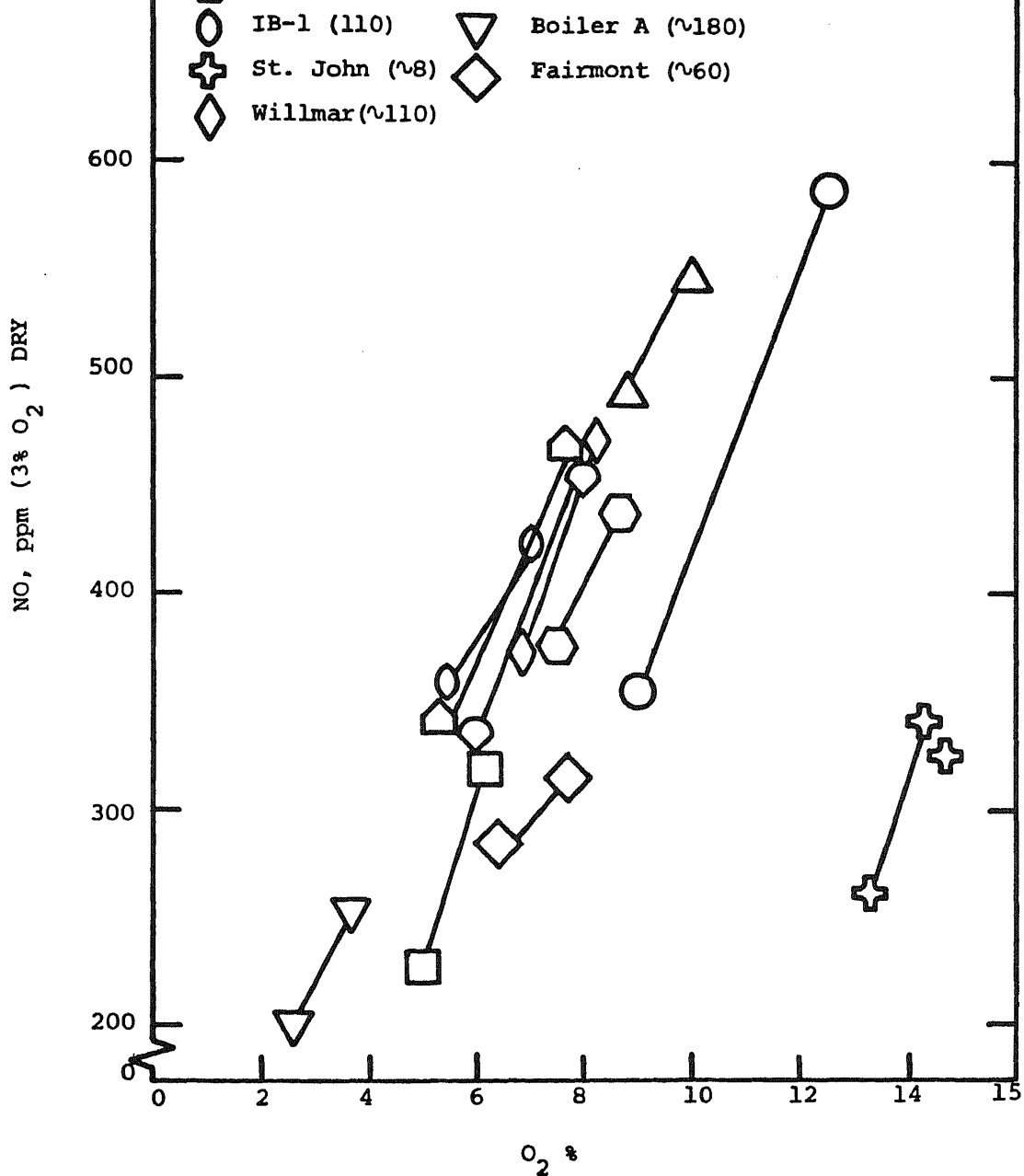
Figure 2. Effect of excess O_2 on NO emissions, spreader stoker units. (Numbers in parentheses indicate operating load in thousand pounds of steam per hour.)

coal units. These reduction potentials are comparable to the results
utility sized units with the same degree of staging (Ref. 1). The wid
application of BOOS to industrial units is questionable due to load r
tions unless modifications to burner and coal preparation systems are

OFA operation has been simulated on stoker units using both existing
overfire air injection systems (installed for increased turbulence in
volatile combustion regions directly above the bed) and through the ai
systems for auxiliary, wall mounted burners. As given in Table 3, the
overfire air injection systems has shown to have little effect on redu
NOx emissions and in fact, increased emissions on an overfed stoker.
auxiliary burners, however, reduced NOx emission levels by 10 to 20%.
data indicate that optimum design of OFA ports for NOx control could s
significant reduction potentials on stoker units. Although data on an
industrial sized suspension fired unit equipped with OFA ports were no
able, the results from utility boiler tests showed reduction potential
15% and 30% for single wall and tangentially fired units, respectively

The data presented in this paper were compiled from field test pro-
grams conducted by KVB under sponsorship of the EPA and DOE (Refs. 3,4
For the most part, the reduction potentials presented in Table 2 perta
conditions at one load point for short duration tests under steady ope
conditions. Examination of these combustion modifications under fluctu
or reduced load conditions over extended periods must be made prior to
full implementation as routine operating procedures.

It should also be emphasized that there are large unit-to-unit varia-
tions in coal-fired industrial boiler NOx emissions, even within the s
boiler design type. This is due to varied boiler geometry with size, a
and coal type. Boiler operating practice, maintenance, coal preparatio
and coal combustion characteristics often vary from plant to plant even
within the same region. Frequently a plant in the northeastern U.S. ma
obtain coal simultaneously from two or three sources. Therefore, it is
unusual to see baseline NOx emissions very by as much as 400 ppm for a
boiler type. Because of this wide variation in baseline emissions, the
is cautioned that the NOx reduction potentials discussed previously can
be guaranteed for all existing units regardless of boiler age, design,
type, etc.
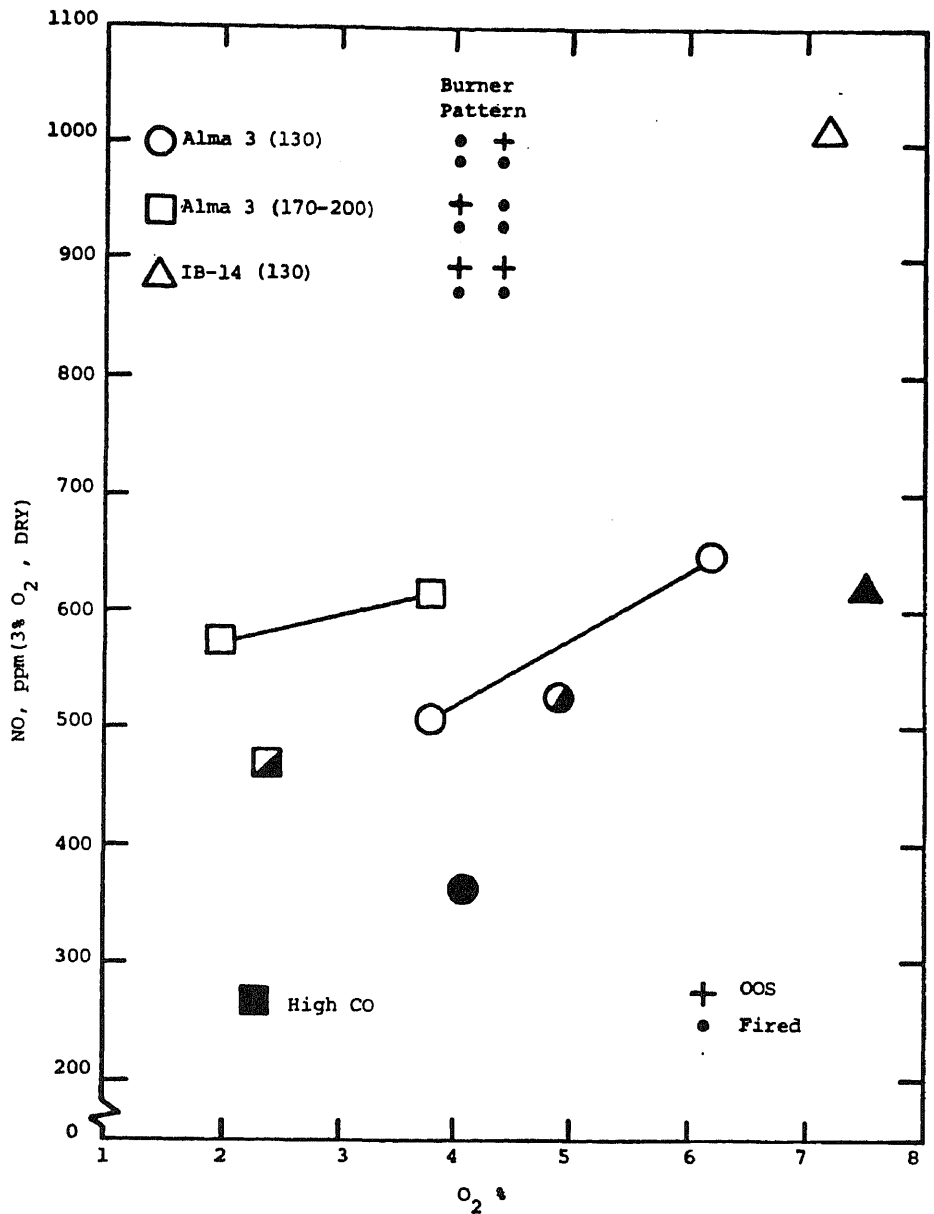
Figure 3.   BOOS operation on single wall-fired pulverized coal
             units for all burners in service (open symbol); no
             air to BOOS (half shaded symbol); and normal air
             distribution to the BOOS (completely shaded symbol).
             (Numbers in parentheses indicate operating load
             in thousand pounds of steam per hour.)

The impact on boiler operations of the initial and long-term use of c
tion modifications is, in many respects, as important as the associat
NOx reduction potential when considering the use of these techniques.
cation of procedures that would seriously affect the safety, reliabil
expected life time of these units would be considered unacceptable by
owners and operators. Although the implementation of staging techniq
industrial units has been applied only on a test basis, experiences f
(1) utility units using BOOS and OFA as normal operating procedures a
industrial units operating with LEA for efficiency reasons can give i
into their possible initial and long term impacts.

Some of the more important concerns and conclusions drawn from a brie
ment of operational considerations are listed below:

- The improper application of LEA or staged combustion can
  result in local reducing conditions that lead to water
  wall corrosion. This potential problem is being exten-
  sively studied on utility boilers by EPA but very little
  industrial boiler work has been performed.

- Low NOx emissions require careful attention to boiler
  maintenance and repair, particularly with regard to
  burners, combustion controls, and other fuel/air equip-
  ment.

- Improved combustion controls and oxygen analyzers may be
  required to maintain optimum low NOx operating conditions.

- Proper implementation of low-NOx boiler operating modes
  need not necessarily lead to increased fuel use or re-
  duced operating efficiency. In most cases, the im-
  proved excess air control offsets the effects of delayed
  combustion resulting in acceptable CO and particulate
  emissions at design efficiency.

- LEA can generally be implemented with a net savings in
  fuel use whereas advanced staging requires hardware and
  auxiliary equipment at 0.1 to 0.3% of the total annual
  cost of operation.

6. ADVANCED CONCEPTS FOR NOx CONTROL
FROM COAL-FIRED INDUSTRIAL BOILERS

Advanced staged combustion low-NOx burner/boiler concepts currently be
developed (Refs. 7,8) for utility boilers have the most promise for ne
pulverized coal industrial boilers. Under government and utility indu
sponsorship, NOx emission levels under 100 ppm have been accomplished

eventually multiple burner units.

 Advanced NOx control concepts for stokers revolve around the use of
overfire air coupled with good undergrate air management to reduce the ove
bed excess air and to lower NOx emissions. Extensive research into contro
NOx emissions from stokers have not been funded but a yet-to-be-awarded
EPA program to examine stoker emissions control design options is expected
to emphasize NOx control.

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SUMMARY

The "Low NO$_x$ Heavy Fuel Combustor Concept Program" is a part of the DOE/LeRC "Advanced Cogeneration Technology Project" (ACT). The program is a contract effort with total funding provided by the Department of Energy, and technical program management provided by NASA LeRC. Main program objectives are to generate and demonstrate the technology required to develop durable gas turbine combustors for utility and industrial applications, which are capable of sustained, environmentally acceptable operation with minimally processed petroleum residual fuels. The program will focus on "dry" reductions of oxides of nitrogen (NO$_x$), improved combustor durability and satisfactory combustion of minimally petroleum residual fuels. Other technology advancements sought include: fuel flexibility for operation with petroleum distillates, blends of petroleum distillates and residual fuels, and synfuels (fuel oils derived from coal or shale); acceptable exhaust emissions of carbon monoxide, unburned hydrocarbons, sulfur oxides and smoke; and retrofit capability to existing engines. Development of these capabilities will be accomplished with a minimum and acceptable sacrifice in other combustor performance requirements. Program goals are intended to be optimistic projections of attainable emission reduction and fuel flexibility. The intent is to generate advanced combustor design technology rather than to verify already available technology. Further, it is intended that the generated technology be retrofittable into existing engines in the near-term. The technology generated will be primarily applicable to near-term industrial and utility engines with pressure ratios of 10:1 or higher, which are suitable for cogeneration applications. The technology will also be applicable to future engines.

INTRODUCTION

This paper describes the Low NO$_x$ Heavy Fuel Combustor Concept Program including its objectives, program plan, schedule, the basis for its emphasis on heavy oil and synfuels, pollution and performance goals, program approaches to pollution reduction, and status to date.

Limited near and mid-term fuel supplies, as well as competition from other users of natural gas, light and mid-distillates could make it attractive for utility and industrial gas turbine manufacturers and users to fire residual oils in their gas turbine

from coal and shale (synfuels). Successful utilization of synfu
represents a still more difficult challenge due to their anticip
increase in impurity content, lower hydrogen-carbon ratio and h
levels of fuel bound nitrogen. Also, under limited circumstance
stationary gas turbines may be required to produce ultra-low
emissions using presently available clean fuels due to stringent
local environmental regulations.

Exhaust emissions from future gas turbines must also meet Federa
emission standards. Oxides of nitrogen emission standards are
difficult to meet with current light distillate fuel oils, and
will become more difficult with residual oils and synfuels.
Water or steam injection has been successful in some installatio
to reduce thermal NO_x formation. However, this approach is clea
not a universally acceptable method since it involves considerab
additional installation and operational costs, and does not redu
NO_x from fuel bound nitrogen. Smoke will also increase with hea
fuel firing as a result of lower fuel hydrogen content.

It appears that substantial reduction of pollutants can be attai
The concepts for pollution reduction now exist. However, althou
the mechanisms of pollution production as well as techniques for
reducing pollutants are generally known, application of these
techniques to specific combustor-engine designs has not yet
demonstrated the anticipated pollutant reductions without com-
promising other combustor parameters. Thus additional technology
is needed to apply these concepts. The Low NO_x Heavy Fuel Combus
Concept Program was initiated to provide a timely evolution of cl
combustors.

The program aim is to develop this required pollution reduction
technology, apply the technology to combustors for industrial and
utility applications, solve interface and performance problems
which low pollutant combustor designs create for engine installa-
tion, and demonstrate the pollution reductions in steady state
and transient testing of development engines.

PROGRAM DESCRIPTION

General

The Low NO_x Heavy Fuel Combustor Concept Program is a multi-year
contract effort funded by the Department of Energy and administer
by the NASA Lewis Research Center. The program's primary objecti
are the following:

heavy oil utilization.

   3.   To permit substitution of heavy oils for light distillate
fuels and natural gas in the near term.

   4.   To permit transition to synthetic liquid fuels when
they become available.

   5.   To investigate and develop the technology required to
achieve ultra-low emissions (one-half the EPA NO_x standard) with
current clean distillate fuels.

   6.   To demonstrate the derived technology in full-scale
engines.

The program is primarily applicable to near-term industrial and
utility engines suitable for cogeneration applications. Additional
applicability is desired for future, higher pressure ratio engines.

Program Plan

It is anticipated that the program will be conducted in three
phases. An overall program diagram is contained in Figure 1.
Program phases are discussed below:

Phase I - Combustion Technology Generation

This phase, which is currently in the process of being implemented,
consists of combustion studies, fuel studies, development of
combustion designs, tests, and retests of multiple combustion
concepts to determine the best concepts for achieving program
objectives. The specific objective of Phase I is to generate the
emission reduction and fuels technology required for future
program phases. This phase, with the exception of the brief
descriptions of Phases II and III presented directly below, is
the subject matter of this paper. As with all program phases,
Phase I will be a contract effort. Multiple contractors are
anticipated.

Phase II - Combustor Screening and Optimization

This phase will consist of incorporating the Phase I combustion
results into engine-combustor hardware, component testing of
promising combustor concepts, iterative redesign and retest of
multiple combustor design approaches to determine the best
combustor approaches for achieving program goals, and development
of combustor liner designs suitable for heavy fuel utilization.
The most promising combustor designs will then be tested further
to develop the required overall performance, durability and engine
adaptability required for engine utilization. Eligible contractors
for this phase will not be restricted to those contractors

Low NO$_x$ Heavy Fuel Combustor Program

Phase I — Technology Generation
- Fuel Process. Qual. Studies
- Design Analysis. Studies
- Combustion Concept Evaluations
- Conceptual Combustor Designs

Phase II — Combustor Optimization
- Combustor Screening Tests
- Adv. Liner Cooling Exp
- Combustor Refinement Tests
- Small-Scale Durability Tests

Phase III — Engine Verification
- Transient Tests
- Alternate Fuels Tests
- Steady State Tests

Competitive Procurement / Open Solicitation

Competitive Procurement / Open Solicitation

Competitive Procurement / Closed Solicitation

Industry Finalization

Industrial Test Bed

Synfuels Combustor Optimization

Utility Test Bed

Ultra-Low NO$_x$ Combustor Optimization

Legend:
- ⬭ — Anticipated program items
- ⬯ — Phase I contract items not part of this procurement
- ⬭ (dashed) — Anticipated program options

Phase III - Engine Verification

This phase will consist of evaluating the best combustor(s) of Phase II as part of a complete engine. The intent is to demonstra in short duration engine testing the emission reductions achieved, fuel flexibility and performance at steady-state and transient conditions. Contractors for this phase will be restricted to those contractors successfully completing the Phase II effort. One or more contractors are visualized.

Since the program emphasizes utilization of minimally processed heavy petroleum fuels, and since burning of petroleum distillates, distillate residual blends and synfuels will be assessed but not optimized, the possibility exists for additional program efforts regarding these latter fuels, which are not a part of the current program. Also, if feasible, additional program efforts involving installation of the derived combustors in field engines for extended evaluation may be undertaken. These potential efforts are contained in dashed lines in Figure 1.

Program Schedule

The planned program schedule is shown in Figure 2. Phase I efforts were initiated in September 1978 with issuance of NASA RFP No. 3-870802. Contract signings are anticipated to occur prior to January 1979, with completion of this phase scheduled to occur within 16 months of contract signing. An approximate 6 month delay is anticipated between the completion of Phase I and the initiation of Phase II, due to procurement procedures. Phase II will be approximately 30 months in duration. It is anticipated that Phase III will be initiated immediately upon completion of Phase II. Phase III will be approximately 16 months in duration.

Fuels Considerations

Fuels availability

Limited near and mid-term petroleum fuel supplies, as well as competition from other users of scarce fuels, could make it attractive for utility and industrial gas turbine manufacturers and users to fire residual oils in their gas turbine equipment. Also, the national goal of reducing dependence on foreign energy supplies in the far-term will make it necessary to use synfuels made from abundant national supplies (Figure 3) of coal and oil shale. Figure 3 also shows the hydrogen to carbon atomic ratio of the various fuel sources. This ratio will be shown in later sections of the paper, to be a major consideration in gas turbine combustor designs. Figure 4 shows the similarity of a heavy petroleum residual and some examples of coal-derived liquids.

Proposed Program Schedule

Description	78	79	80	81	82	83
Phase I:		■				
Phase II:				■	■	■
Phase III:						■

Figure 3

U.S. Remaining Fuel Resources
(Approximate)

	10^{15} BTU	H/C Ratio
Petroleum	700	2.00
Synthetic Fuels*		
Tar Sands	100	1.75
Oil Shale	20,000	1.90
Coal	90,000	0.75

Liquid Fuel Consumption US 40 x 10^{15} BTU/Year

*Fossil Fuels Derived from Other than Petroleum

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Figure 4

Liquid Fuels for Directly Fired Engines

| Key Characteristics | Todays Std. | Near-Term Heavy Petroleum | Mid-Term Minimally Processed Coal Deriv | | | | | |
| | =2 Distillate | Residuals | *Exxon Donor Solvent | *H-Coal | | Resid. | S... |
				*Light Dist'te.	Heavy Dist'te.		l-Light Dist'te.
Fuel Bound Nitrogen (Wt. %)	.06	.05 to .5	.7	0.42	1.01	1.3	1.5
Hydrogen/Carbon (Atomic Ratio)	1.8	1.3	1.09	1.38	1.01	1	.8
Ash (Wt. %)	—	.05	.03	Nil	Nil	0.2	0.2
Sulfur (Wt. %)	0.5	0.5 to 2.7	0.6	0.18	0.22	0.48	0.8
Pour Point (°F)	-10 to +20	+40 to +70	+20	-100	+86	+115	+500

and acceptable durability will help determine the economic feasibility of synfuels. To be economically competitive, synthetic liquids must be minimally processed, i.e., hydrogenation of coal-derived crudes must be kept to an absolute minimum.

Phase I Test Fuels

Three test fuels have been specified for Phase I. These fuels are described in Table I. Fuel A is a petroleum distillate simulating Diesel #2 properties. The objective of testing with this fuel will be to achieve ultra-low NO_x which is defined as one half the applicable EPA standard. Ultra-low NO_x combustors are required in areas where local regulation, more stringent than the EPA standard are in effect.

Fuel B is a petroleum residual fuel and is the major basis for combustion design in this program. Correspondingly, test efforts will emphasize utilization of this fuel. Fuel C is also a petroleum residual, with degraded properties as indicated by the reduced hydrogen-carbon ratio. The intent of testing with this fuel is to simulate operation with synfuels derived from coal or shale. It is anticipated that if available in sufficient quantity, synfuels will be substituted for fuel C during the program.

In addition to testing with the fuels defined above, additional fuel tests will also be conducted in Phase I. Test fuels B and C will be doped with pyridine to investigate combustion approaches for reducing fuel bound nitrogen conversion. Levels up to 0.5% by weight of fuel bound nitrogen will be investigated with fuel B. Levels up to 1.2% by weight of fuel bound nitrogen will be investigated with fuel C.

In addition, blends of fuel A with fuel B, and blends of fuel A with fuel C will also be investigated. The objectives of these tests are: to determine the tradeoffs concerning fuel quality and its effects on combustor emissions and performance.

Several of the difficulties anticipated to be encountered in burning minimally processed heavy fuels are listed in Table II. Increased alkali metal content of heavy fuels are anticipated to create corrosion and deposition problems on combustor liners and turbine blades. Increases in boiling range increase tendencies of gum formation and carbon deposition on fuel nozzles and combustor liners. Reduced hydrogen content causes increased radiation during combustion, thus producing increased heat loading to combustor liners and adversely affecting combustor

SPECIFICATIONS	PROPOSED TEST METHOD	PETROLEUM DISTILLATE	PETROLEUM RESIDUAL	PE... RE...
COMPOSITION:				
HYDROGEN, WT. %	NMR	12.8±0.2	10.8±0.2	10...
SULFUR TOTAL, WT. %	ASTM D129	0.8 max.	0.8 max.	0...
*NITROGEN TOTAL, WT. %	Kjeldahl	0.1 max.	0.2 max.	0...
HYDROCARBON COMPOSITIONAL ANAL.	GCMS	REPORT	REPORT	RE...
ASH, WT. %	ASTM D482	20 ppm max.	0.04 max.	0...
ASH MELT TEMPERATURE, °F	TBD	REPORT	REPORT	RE...
AROMATICS TYPE:				
AROMATICS TOTAL, VOL. %	ASTM D1319	REPORT	REPORT	RE...
SATURATES	TBD	REPORT	REPORT	RE...
OLEFINS	TBD	REPORT	REPORT	RE...
NAPHTHALENES	TBD	REPORT	REPORT	RE...
CARBON RESIDUE:				
ON 10% WT., %	ASTM D524	REPORT	REPORT	RE...
ON 100% WT., %	"	REPORT	REPORT	RE...
WATER & SEDIMENT, VOL. %	TBD	REPORT	REPORT	RE...
VOLATILITY:				
DISTILLATION TEMPERATURE, VOLUME RECOVERED, °F --- max.				
INITIAL BOILING POINT	ASTM D86	REPORT	REPORT	RE...
10%	"	425±25	600±50	60...
50%	"	REPORT	REPORT	RE...
FINAL BOILING POINT	"	650±50	1000±100	10...
RESIDUE	"	REPORT	REPORT	RE...
FLASH POINT, °F	ASTM D93	REPORT	REPORT	RE...
GRAVITY, °API	ASTM D287	REPORT	REPORT	RE...
FLUIDITY:				
POUR POINT, °F	ASTM D97	20 max.	50 max.	50...
VISCOSITY AT 100 °F:				
KINEMATIC, cS	ASTM D445	REPORT	REPORT	RE...
SAYBOLT UNIVERSAL, SEC.	ASTM D88	REPORT	REPORT	RE...
COMBUSTION:				
NET HEAT OF COMBUSTION, BTU/LB	ASTM D2382	REPORT	REPORT	RE...
THERMAL STABILITY:				
JFTOT, BREAKPOINT TEMPERATURE, °F (TDR, 13; ΔP, 25 mm)	ASTM D3241	REPORT	REPORT	RE...
TRACE METAL ANALYSIS: ppm				
V	TBD	REPORT	REPORT	RE...
Ni	"	REPORT	REPORT	RE...
Na	"	REPORT	REPORT	RE...
K	"	REPORT	REPORT	RE...
Mg	"	REPORT	REPORT	RE...
Ca	"	REPORT	REPORT	RE...
Pb	"	REPORT	REPORT	RE...
Cu	"	REPORT	REPORT	RE...
Fe	"	REPORT	REPORT	RE...
Si	"	REPORT	REPORT	RE...
Zn	"	REPORT	REPORT	RE...
Ba	"	REPORT	REPORT	RE...
Mn	"	REPORT	REPORT	RE...
Mo	"	REPORT	REPORT	RF...
Ti	"	REPORT	REPORT	RE...

* Additional Nitrogen concentrations to be investigated are defined in Tasks I
  of Exhibit "A".

Table II

Fuel Considerations & Impacts

Parameter	Fuel Types			Effect
	Current # 2	Heavy Oils	High F.B. Nitrogen	
Alkali Metal Content	Low	High	Higher	Corrosion & Deposition
Typical Boiling Range °R	380-650	600-1000	600-1000	Gumming & Carbon Formation
Hydrogen Content Wt. %	12.2-13.2	10-12.5	9-12.5	Luminosity + Smoke
Thermal NO_x	High for All in Relation to Stds.			
F.B. Nitrogen % Wt.	0-0.2	0-0.5	0.5-1.2	NO_x Conversion

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Emission Goals

Program emission goals are based on EPA Proposed Regulation, F.R. 40 CFR Part 60 and are subject to all of the constraints and corrections contained in this citation.

The emission goals are contained in Table III. Engine operating conditions for which the goals apply are discussed in a subsequent section. These operating conditions incorporate all engine power levels for load following engine-combustors.

The sulfur dioxide goal represents a limitation on fuel sulfur, since all of the fuel sulfur is transmitted through the combustor. It is included here for consistency with the referenced citation. Subsequent program phases will address the question of fuel sulfur level regarding its removal either upstream or downstream of the combustor. Smoke is not currently regulated by the EPA. Rather, it is subject to local regulation. An S.A.E. number of 20 is consistent with advanced state-of-the-art combustor design practices.

Achievement of the Oxides of nitrogen (NO_x) standard represents the most difficult program goal for achievement. Water or steam injection to reduce oxides of nitrogen by reducing flame temperatures will not be relied upon as a control device in this program. "Dry" reductions of oxide of nitrogen through combustor design will be sought. At present, the technology required to control of NO_x through combustor design is not available, even with clean distillate fuels. The current NO_x emissions will have to be reduced by a factor of 2 to 3 to meet goals shown in Table III. There are also indications that achievement of the NO_x standard value will be more difficult to achieve with heavy fuels. This is shown in Figure 5.

Fuel bound nitrogen levels in the fuel also make achievement of the NO_x standard more difficult. Current EPA regulations permit correction for fuel bound nitrogen up to 0.25%. Fuel bound nitrogen levels in excess of 0.25% must be compensated for by reducing the conversion of fuel nitrogen into NO_x. Typical fuel bound nitrogen conversion data, for a current production industrial engine are shown in Figure 6.

It is anticipated that additional emission goals will be added to future program phases. For example, a particulate goal is anticipated for program Phases II and III.

Table III
Emission Goals

Pollutant	Maximum Level	Operating Cond.
Oxides of Nitrogen[1]	75 PPM @ 15% 0^2	All
Sulfur Dioxide[1,2]	150 PPM @ 15% 0^2	"
Smoke[3]	S.A.E. Number = 20	"

Notes:

1 — EPA Proposed Regulation, F.R. 40 CFR Part 60

1,2 — Limit of Fuel Sulfur Content

3 — No EPA Regulation, Local Rules

Figure 5

Thermal NO$_x$ Considerations
Typical Combustor
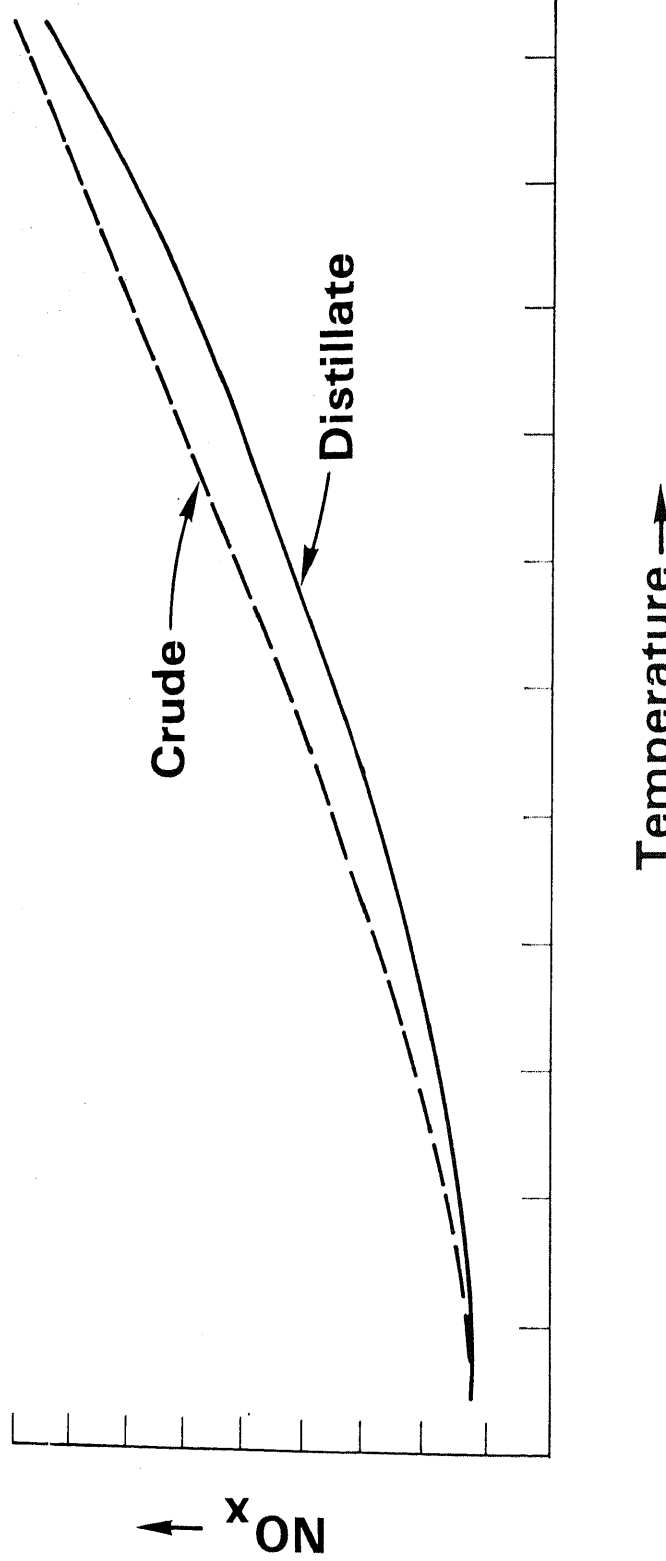
Figure 6
Fuel Bound NO$_X$ Considerations

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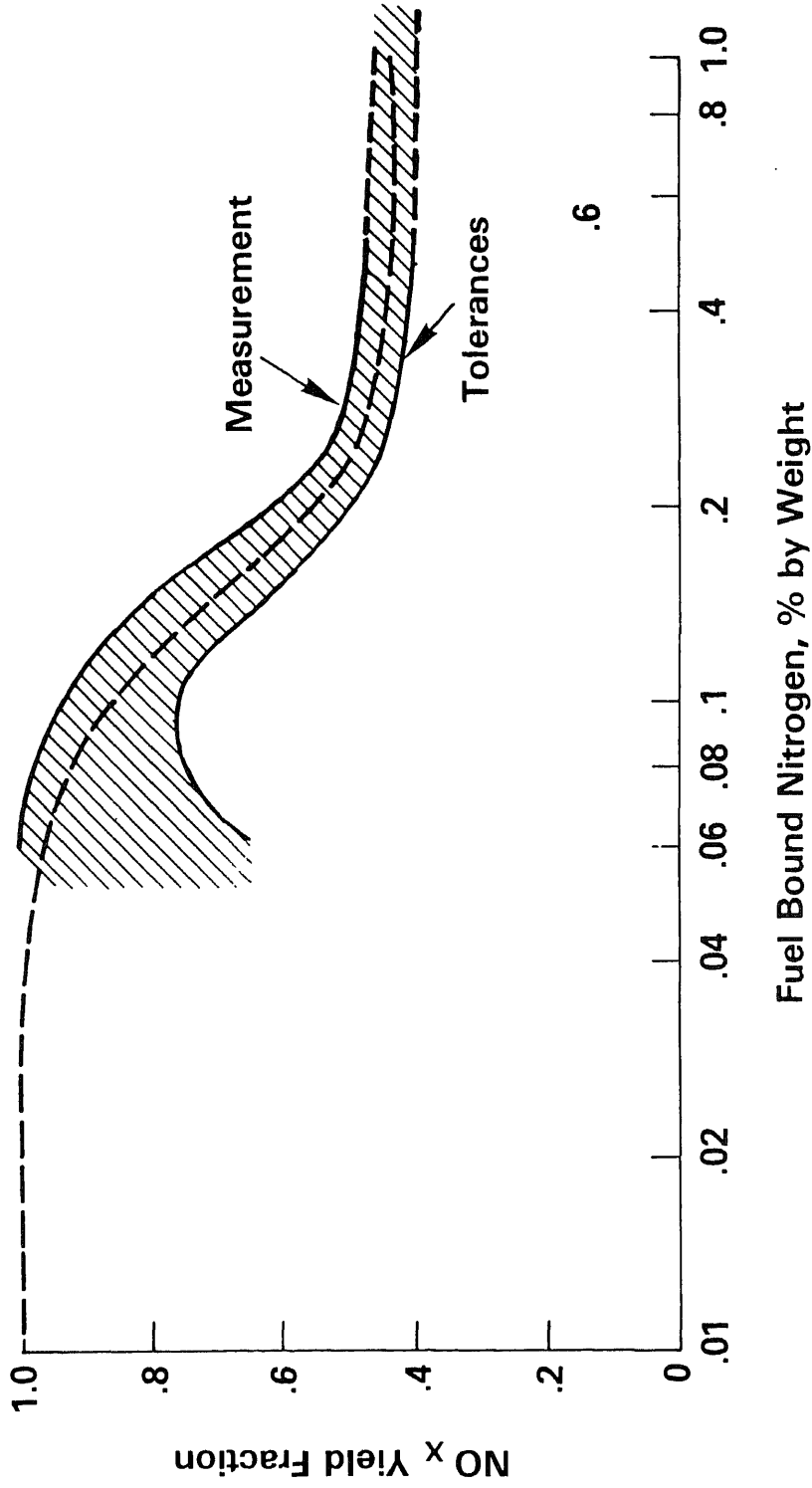
can be increased in pursuit of the pollution goals.

The combustion efficiency goal effectively imposes maximum
allowable levels of unburned hydrocarbon (HC) and carbon monoxid
(CO), since levels of these emissions are direclty relatable to
combustion inefficiency. Conversely, program measurements of
combustion efficiency are specified to be recorded through
emission level determinations. Current combustors operate very
efficiently at high engine power points (50% of engine rated
power level and above). However at lower engine power levels,
especially at spinning idle conditions, combustion inefficiencie
occur with most current engines.

Test Conditions

Combustor test conditions over which the emission and performance
goals apply are contained in Table V. Implicit in the selection
of these test conditions is a requirement for load following
capability. Load following capabilities are deemed to be
necessary for this program because cogeneration applications
for the derived technology are visualized. Most industrial and
utility gas turbine engine combustors operate efficiently at
a nominal base load condition and somewhat less efficiently
at off-design or lower power conditions. The requirement that
engine combustors operate efficiently over a load range is a
significant requirement. To achieve this type of operation,
combustor performance must be optimized for a variety of
combustor inlet conditions, including those of low temperature,
pressure and fuel/air ratio.

Combustor Considerations and Design

Advanced combustor designs will be emphasized in the Phase I
program. A non-inclusive list of pollution reduction techniques
which will be investigated in the program are contained in
Table VI. Included in the table is the pollutant of concern
and the corresponding pollution reduction concept.

Control of thermal NO_x involves reduction of flame temperatures
below 3000°F and short residence times of combustion gases at
high temperatures. Simultaneous control of thermal NO_x and smoke
additionally requires uniform distribution of fuel and air, and
avoidance of excessively high fuel rich zones. Control of the
conversion of fuel bound nitrogen into NO_x involves burning under
fuel rich conditions or, correspondingly, oxygen lean conditions.

The technology developed in Phase I should be applicable to all
types of gas turbine combustors. An illustration of these

Table IV
Performance Goals

Combustion Efficiency*	>	99% at All Operating Conditions
Total Pressure Loss	<	6% at Base Power Load
Outlet Temperature Pattern Factor	=	0.25 at Base Load & Peak Load Power
Combustor Exit Radial Temperature Profile	=	Equivalent to Production Comb. Values

*Calculated on a Deficit Basis from Measurements of Co, THC & CO_2

Table V

Proposed Combustor
Test Conditions

Cold Start

Spinning Idle

30% Rated Power

50% Rated Power

70% Rated Power

80% Rated Power — Nominal Base Load Condition

$00% Rated Power — Peak Load Condition

Parametric Variation

Table VI

Pollution Reduction Techniques

Pollutant	Reduction Concept
Thermal NO$_x$ Reduction	Diluent Injection into Burning Zone Quick Quench Catalytic Combustion
Thermal NO$_x$ and Smoke Reduction	Premixed/Prevaporized Burning Ultra Lean Burning Advanced Fuel Injection Multiple Fuel Utilization
Organic NO$_x$ Conversion Reduction	Rich Burning with Controlled Quench

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in Figure 8. Single stage combustors represent current technol
Multi-zone combustors represent advanced technology which is
currently being evolved for both ground based and aircraft
gas turbine combustors. Multi-zone designs, while considerably
more complex than current designs, provide additional degrees o
flexibility in staging fuel and combustion to optimize performa
for a variety of test fuels, emission and performance constrain

CONCLUDING REMARKS

It is anticipated that Phase I of this program will provide the
technology base for future program phases. Specifically it is
anticipated that Phase I will provide the following:

    1. Definition of the most promising combustor design
approaches for utilizing heavy fuels derived from petroleum and
other sources.

    2. Definition of tradeoffs involving fuel quality and
combustion and emission performance.

    3. Identification of realistic fuels for future program
phases.

    4. Identification of engine applications for the derived
technology. This will include preparation of conceptual engine-
combustor designs.

    5. Identification of development efforts required to
utilize minimally processed heavy fuels in sub-component
combustor areas such as fuel systems, liners, etc.

Figure 7

Potential Combustor Types

On Engine

Off Engine

Can

Can-Annular

Annular
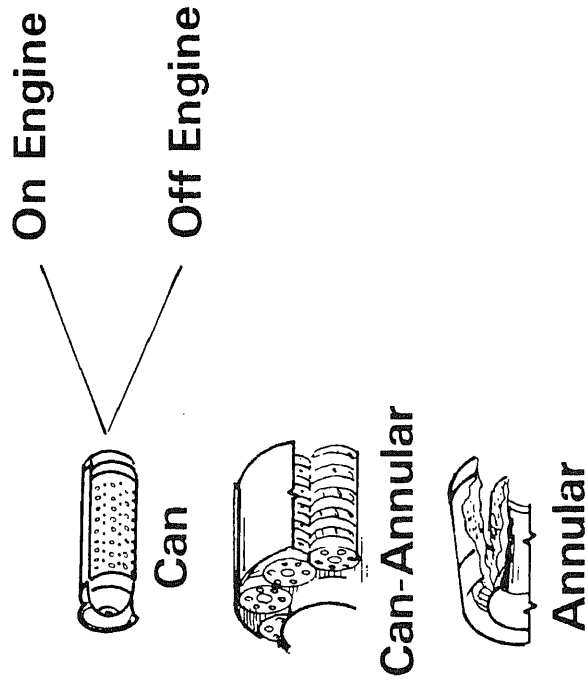
Combustor Designs
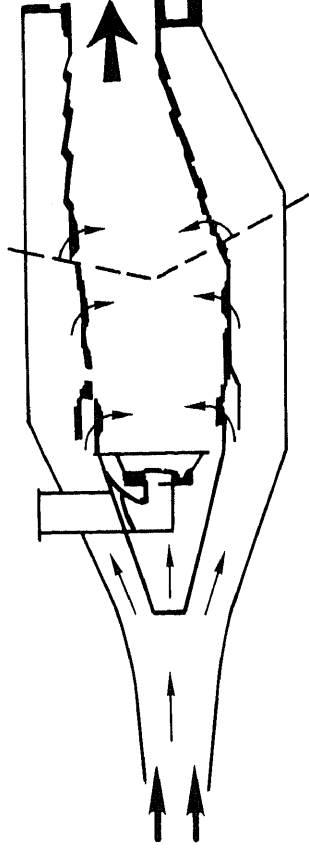
Single-stage

Multi-zone

P. Gorman

P. Reider
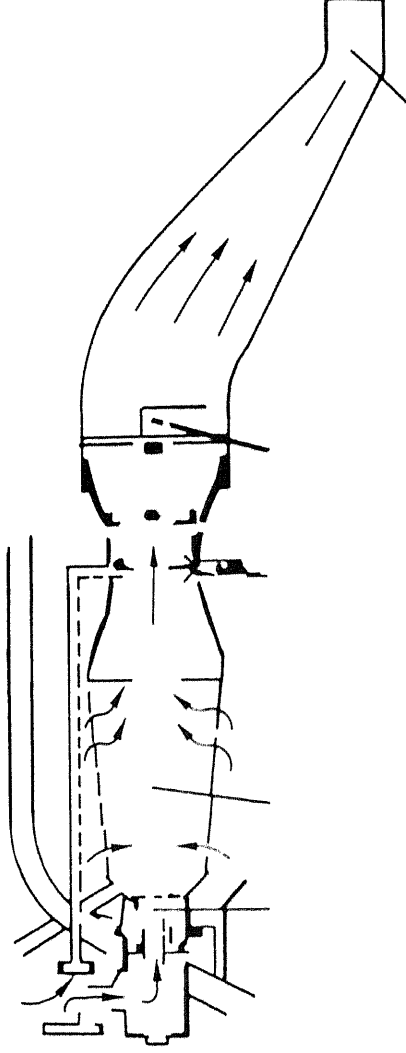
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

ABSTRACT

        Midwest Research Institute conducted a project under contrac
with Argonne National Laboratory to assess the economic and energy im-
pacts of particulate control systems in coal-fired power plants. The
assessment was based on major functional variables such as plant size
(100 to 1,000 MWe), location, coal type, and emission standards. The
work resulted in the generation of algorithms to predict equipment
cost, installation costs, and energy usage for various particulate con-
trol devices. The devices considered were: electrostatic precipita-
tors (hot-side and cold-side); fabric filters (reverse air and shaker
types); and wet scrubbers.

        A boiler performance model was developed using variables suc
as plant size, coal characteristics, etc. The output from this model
(i.e., flue gas flow rate, grain loading, etc.) was utilized in contro
device performance models to generate required design and operating
parameters for the control systems under study. The design and operat
ing parameters were then used in the cost models that were also devel-
oped in this program.

        The cost models aggregate three cost items: (a) the first
costs (capital investment); (b) total first-year annualized costs; and
(c) the integrated cost of ownership and operation of the control
equipment over an assumed plant lifetime of 30 years. The models have
been programmed for speedy computation. However, the algorithms are
easily solvable with a hand calculator. In addition, suitable guide-
line values have been provided for independent variables wherever nec-
essary. Case studies are presented to demonstrate results of the
models.

new plants, especially in view of stringent emission regulations (e.g., 0.03 lb/10^6 Btu). Since there are a number of control device options available for particulate control, there is a need for being able to estimate the economic and energy impacts of each control option for a given set of plant specifications. Realizing this need, Argonne National Laboratory contracted with Midwest Research Institute (MRI) to develop the necessary algorithms to predict equipment cost, installation costs, and energy usage for five particulate control devices: electrostatic precipitators (ESPs) including hot-side and cold-side, fabric filters, both reverse air and shaker type, and wet scrubbers.

The methodology used for the model development is presented in Figure 1. A set of algorithms was developed to quantify the aspects of a boiler that relate to the design of fly ash control equipment. This boiler performance model utilizes input values such as plant size, coal characteristics, and boiler type for the computation of parameters critical to control devices (e.g., flue gas flow rate, uncontrolled particulate emissions, etc.). Thereafter, algorithms were developed that use the information generated by the boiler performance model, plus the emission limit specified, to compute various control device design parameters (e.g., collecting area for an ESP). A subsequent set of algorithms use these device parameters to compute equipment and operating costs and energy usage. The breakdown of cost items considered is presented in Figure 2. The cost and performance algorithms discussed in this paper are composites of relationships published in the literature and additional information obtained as part of this project.

The following sections of this paper describe the salient features of the boiler performance model as well as the control device performance and cost models, including the various cost and energy consumption factors that were considered. The final section presents a summary of the results obtained from these models when applied to a hypothetical 500-MWe plant at three different geographic locations, burning three different coals.

Total Use and Ownership Cost
- Operation
  - Material
  - Utility Consumption
  - Direct Labor
- Maintenance
  - Material Consumption
  - Direct Labor
- Financial Charges
  - Capital Charges
    - Depreciation
    - Interest on Debt
    - Investment Tax Credit
  - Misc. Charges
  - Taxes, Insurance, Contingency
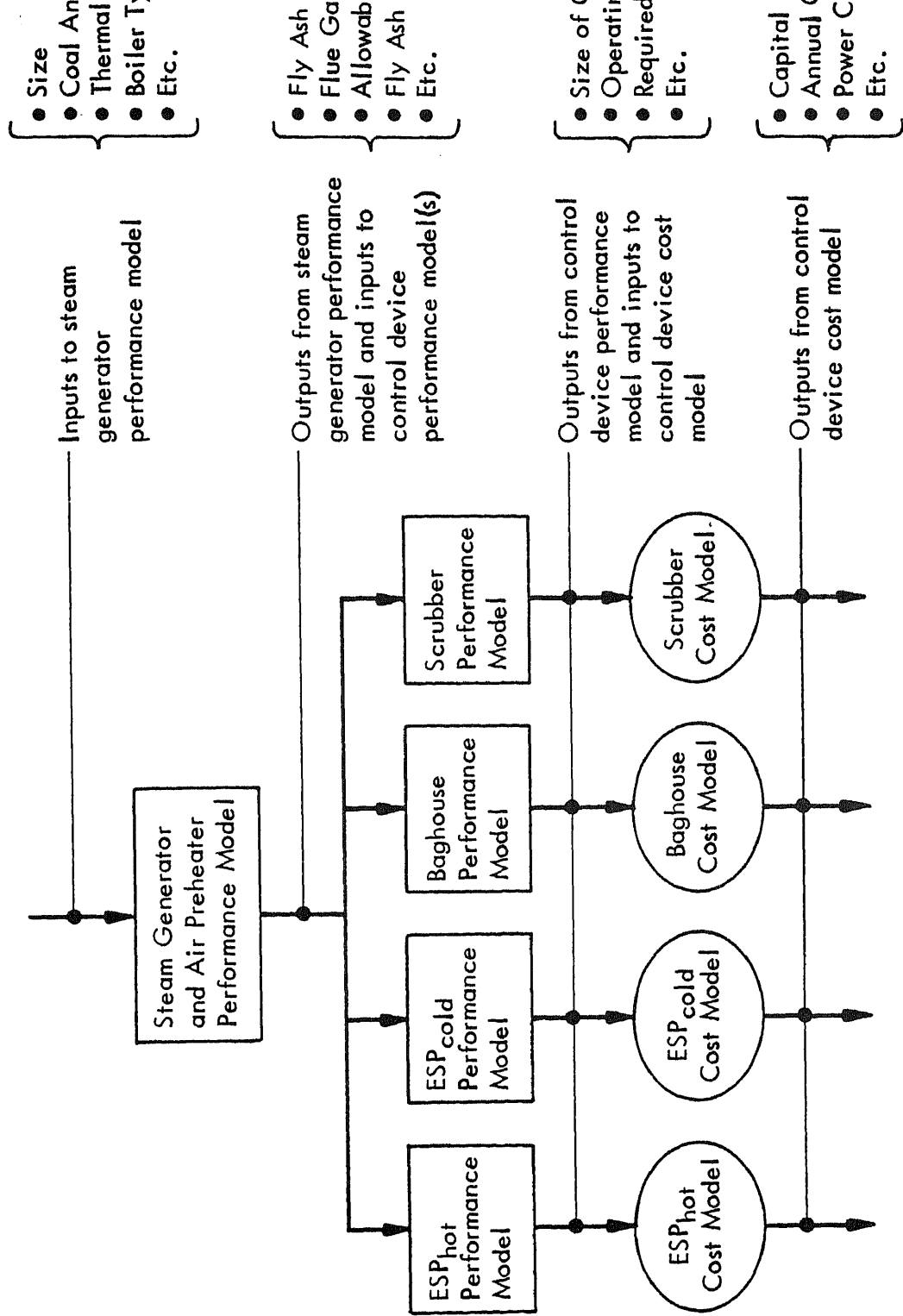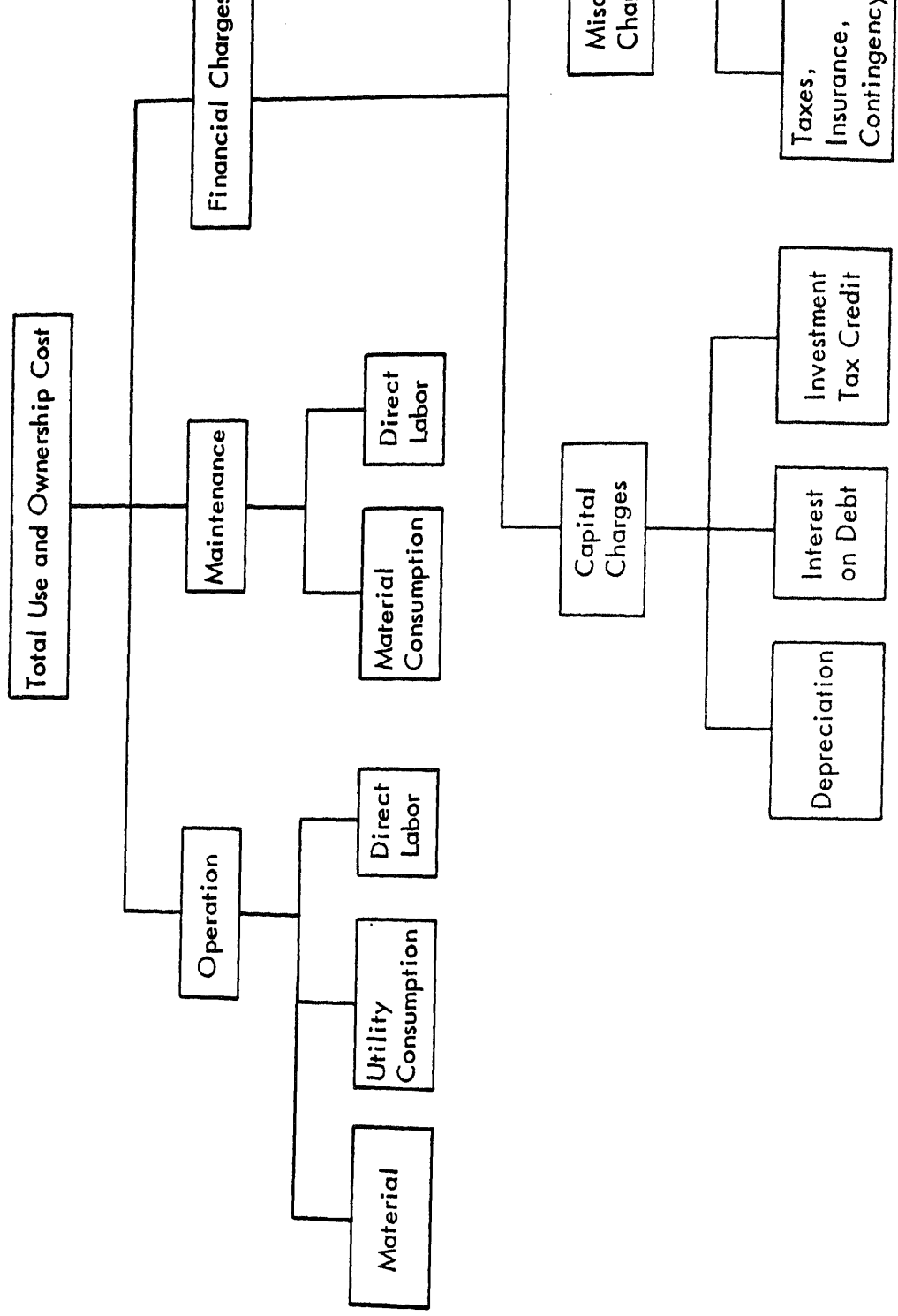
number of parameters for which the user may not know the actual values, suggested default values are given. This procedure is also followed for many of the other algorithms developed in this project.

Table 1. Steam Generator Performance Model Inputs

Description	Unit	Default Value
Generation rate	MWe	-

Boiler type
  Pulverized coal dry bottom or wet bottom,
  or cyclone
	-	-

Plant location, state	-	-
Heating value of coal	Btu/lb	-
Plant thermal efficiency, decimal fraction	-	0.388

Flue gas temperature
  At preheater inlet
  At preheater outlet
	°F	
		700
		350

Boiler emission factor	lb fly ash/lb of ash in coal	
For pulverized coal dry bottom boiler		0.85
For pulverized coal wet bottom boiler		0.65
For cyclone boiler		0.10
Excess combustion air, decimal fraction	-	
For pulverized coal boilers		0.20
For cyclone boilers		0.15
Coal analysis, decimal fraction for N, C, H, S, and H_2O	-	-

. Coal firing rate, tons/hr,

. Flue gas flow rate, acfm,

. Heat input rate, 10^6 Btu/hr,

. Mean diameter and standard deviation of fly ash particl
  size distribution, and

. SO_2 flow rate in flue gas, lb/min.

The above parameters then constitute the inputs to the var
control device design models.

Before describing the control device design and cost model
an individual basis, several aspects that the models have in common
identified.

First, the algorithms generate costs in 1978 dollars, but
provisions have been made for the user to modify the costs to any ye
dollars beyond 1978 by using projected cost indices.

Second, a table is provided in the original report[1] that
allows for state-to-state variations in costs, including wage rates,
power costs, construction costs, and land acquisition costs. In the
cost models, which may be adjusted for different locations, an averag
wage of $7.41/hr was used for utility workers and an average land cos
of $10,000/acre.

Third, the cost of the control devices was amortized on an
accelerated basis over a 5-year period, per the Tax Reform Act of 197
Interest was assumed to be 8%, based on the prime rate, but the user
may specify other values. Also, an investment tax credit of 10% was
applied for the first year of operation.

Fourth, one of the cost criteria used in the overall econom
analysis was the total cost of owning and operating the plant over a
specified plant lifetime (e.g., 30 years) in terms of first-year dol-
lars. This computation requires several economic projection figures,
including discount rates for present value analysis and increases in

report.

The performance and cost models developed for each control device contain several algorithms. The following sections discuss the more important ones and their development.

A. Cold-Side ESP

1. Performance model: The familiar Deutsch equation was used for "sizing" a cold ESP. This equation requires knowing the particle migration velocity, so a modified form of algorithm developed by Southern Research Institute (SRI)[2] was used which computes the migration velocity parameter as a function of:

.   Type of boiler,
.   Current density,
.   Power density,
.   Voltage,
.   Number of electrical sets,
.   Moisture content of flue gas,
.   Sulfur and ash in coal,
.   Flue gas temperature, and
.   Uncontrolled fly ash loading.

Since all of the above variables may not be known by the user suggested default values are given, some of which are selected on the basis of the sulfur content of the fuel.

The Deutsch equation uses the migration velocity along with the gas flow rate and the required collection efficiency to compute the collecting area. The collecting area then becomes a major input parameter for the ESP cost model.

2. Cost model: Equipment and installation costs for the cold ESP are computed using algorithms developed from a model by Bubenick[3] and data reported by the Industrial Gas Cleaning Institute (IGCI).[4] The following equations result for equipment and installation costs:

$$EC_C = 45.94 \ A_{CP}^{0.88}$$

$$IC_C = 23.58 \cdot ACF \cdot A_{CP}^{0.896}$$

IC_C = cold ESP installation cost, 1978 dollars

A_{CP} = collecting plate area, ft^2

ACF = area construction factor

The cost model also contains several other cost algorithms for computing:

- Ash handling equipment cost,
- Ash handling installation cost,
- Land cost,
- Electrical capacity charge,
- Power cost,
- Operating labor cost,
- Maintenance material cost, and
- Maintenance labor cost.

The electrical capacity charge in the above list represents the cost of additional power plant capacity that is required to meet the electrical requirements of the control device. The value basis used is \$900/kw.

In addition to the financial charges discussed earlier (depreciation and investment tax credit), the cost models also include overhea taxes, insurance, and contingency.

B. Hot-Side ESP

1. Performance model: The hot-side ESP model also relies on the Deutsch equation for computing the collecting plate area. Since available data on hot ESP were not sufficient to develop an algorithm for migration velocity, the user must specify a migration velocity or select one of the suggested default values, which are as follows:

0.30 ft/sec for pulverized coal boiler burning coal with > 1% sulfur

0.25 ft/sec for pulverized coal boiler burning coal with < 1% sulfur

0.18 ft/sec for cyclone boiler

$$IC_H = 9.588 \cdot ACF \cdot A_{HP}^{0.952}$$

where:

EC_H = hot ESP equipment cost, 1978 dollars

IC_H = hot ESP installation cost, 1978 dollars

A_{HP} = collecting plate area, ft^2

ACF = area construction factor

Algorithms were also developed for other cost items listed above. These algorithms are similar in form to those for the cold ESP; however, one additional factor included for the hot ESP is heat loss from the ESP due to higher operating temperature. It was assumed that this heat loss results in additional fuel consumption to maintain the power output. Since data collected in this project indicated that the average drop in the flue gas temperature across a hot ESP is about 7°F, this was the value used in an algorithm to compute the annual cost for the additional fuel. The cost of the fuel is based on a default value of $1.75/$10^6$ Btu. The annual cost of this heat loss is a significant portion of the total annual operating cost for a hot ESP.

C. Fabric Filters

1. Performance model: Performance and cost models were developed for both reverse flow and shaker type baghouses, the costs based primarily on cloth area required. This parameter is calculated i the performance models using an air-to-cloth ratio specified by the user, or a default value of 2.0 acfm/ft^2 for reverse flow type and 2.8 acfm/ft^2 for shaker type. These are net values, allowing for one compartment being off-line for cleaning and one off-line for maintenance.

The pressure drop through baghouses is considerably higher than in ESPs, and it significantly affects operating costs. Therefore, algorithms were developed to compute the pressure drop using informatic from baghouse manufacturers and the recent TVA/Shawnee project.[5]

verse flow and ~~~~

$$EC_{RB} = 16.6 \; GCA^{0.966}$$

$$EC_{SB} = 21.08 \; GCA^{0.966}$$

where:

EC_{RB} = equipment cost, reverse flow baghouse, 1978

EC_{SB} = equipment cost, shaker baghouse, 1978 dollar~

GCA = gross cloth area, ft^2

Gross cloth area is also the major parameter used installation costs for the baghouses. Many of the other equ operating costs are similar to the ESP model. But an additic item considered for the baghouses was bag replacement. Avai on replacement costs were used to develop the following equa this cost item:

$$RBC_{RB} = 0.78 \; GCA$$

$$RBC_{SB} = 0.63 \; GCA$$

where:

RBC_{RB} = cost of replacement bags, reverse flow bag 1978 dollars

RBC_{SB} = cost of replacement bags, shaker baghouse, dollars

GCA = gross cloth area, ft^2

It was assumed in the default condition that all b be replaced every 3 years, although the user may specify oth Additionally, equations were developed for bag replacement l

The algorithms developed for the financial charges to those for ESP.

1. <u>Performance model</u>: The model developed (for venturi scrubbers) considers fly ash removal only and excludes those scrubber systems in which particulate and SO_x control are achieved simultaneously. (However, it does consider the neutralization requirements due to the absorption of certain amounts of SO_x.) Development of the scrubber performance model was based on work by Calvert[6,7,8] and involves a trial and error procedure to determine the pressure drop and liquid-to-gas ratio required. Several simplifying assumptions were made in developing the design equations. Some of these assumptions relate to the specific application area of the model, viz., fly ash control in coal-fired boilers.

2. <u>Cost model</u>: Total equipment cost for the venturi scrubber was derived from costs reported in the literature. Regression analysis indicated that these data can best be expressed by:

$$EC_S = 1.59 \ Q_S^{1.062}$$

where:

EC_S = equipment cost, scrubber, 1978 dollars

Q_S = saturated flue gas flow rate, acfm

Several other cost algorithms were developed to determine:

.   Installation cost,
.   Land cost (for the scrubber and for a settling pond),
.   Power usage,
.   Electrical capacity charge,
.   Operating labor cost,
.   Material cost (lime and water),
.   Maintenance material,
.   Maintenance labor, and
.   Flue gas reheat cost.

Like the hot ESP heat loss, the flue gas reheat is an additional cost associated with wet scrubbers. An algorithm was developed to calculate the cost for equivalent fuel. The algorithm assumes an energy cost of $1.75/10^6$ Btu and a reheat requirement of 50°F, unless the user specifies otherwise.

This model also includes all the financial charges discussed above.

All of the perfor[...]

case studies. The basic system characteristics pertaining to th[...]
cases are shown in Table 2. These input parameters were used i[...]
case studies to derive design and/or size specifications for eac[...]
the control devices based on the models described in the earlie[...]
(Table 3).

Table 4 presents the cost comparisons for the control[...]
resulting from the calculations for the three case studies. Tab[...]
shows that the relationship of cost factors for the different co[...]
devices is the same; i.e., for any single case, the cost ranking[...]
same regardless of which cost factor is used. It is found that [...]
ESP is the least expensive control method for the cases of mediu[...]
high sulfur coal. In the case of low sulfur coal, however, the [...]
is shown to be more expensive than a hot ESP or either of the fa[...]
filters. Comparing the hot ESP and baghouse, the former is more[...]
effective for low sulfur coal. In medium and high sulfur coal [...]
the hot ESP is more expensive than the cold ESP but less expensi[...]
either of the baghouses. The cost of the baghouse remains fairl[...]
pendent of coal characteristics. Clearly, the high operating co[...]
equipment cost of scrubbers make them uneconomical if they are [...]
only for particulate control.

A comparison of energy consumption factors for differe[...]
trol devices is presented in Table 5. In terms of total energy [...]
tion, the results show that a cold ESP ranks as the most energy-[...]
device, followed by a baghouse and then a hot ESP. Particulate [...]
are shown to be the highest energy consumers. From the data in [...]
it is evident that the high energy consumption of scrubbers and [...]
is, in part, due to stack gas reheat and heat losses, respective[...]
example, in the case of a scrubber with Pennsylvania coal, 17.64[...]
energy are required for stack gas reheat in comparison to 16.76[...]
energy for the operation of the scrubber.

Table 2. Fundamental System Characteristics of Sample Gases

System Characteristic Items	Sample Case 1	Sample Case 2	Sample Case 3
Plant site (mine-mouth plant)	Rosebud County, Montana	Franklin County, Illinois	Westmoreland County, Pennsylvania
Coal source	Rosebud County, Montana	Franklin County, Illinois	Westmoreland County, Pennsylvania
Coal cleaning	Level 1	Level 1	Level 1
Coal characteristics[a]			
Moisture	13.6	4.10	5.0
Ash	7.6	7.20	22.0
Sulfur	0.60	2.58	3.23
Carbon	60.00	72.30	60.00
Hydrogen	5.4	5.4	5.4
Nitrogen	1.6	1.6	1.6
Heating value, Btu/lb	10,116	12,768	10,912
Regulations	New Source Performance Standards (NSPS), i.e., 0.03 lb/10^6 Btu	New Source Performance Standards (NSPS), i.e., 0.03 lb/10^6 Btu	New Source Performance Standards (NSPS), i.e., 0.03 lb/10^6 Btu
Boiler type	Pulverized coal-fired dry bottom boiler	Pulverized coal-fired dry bottom boiler	Pulverized coal-fired dry bottom boiler
Capacity[b]	500 MWe total	500 MWe total	500 MWe total

[a]Weight percent as received.

[b]The power consumed internally for the operation of the control equipment is not considered.

Parameter	Cold ESP			

Low Sulfur Montana Rosebud Coal (Case 1)[a]

Parameter	Cold ESP			
Migration velocity, ft/sec	0.110	0.25	–	–
Collecting plate area, ft^2	1,330,281	840,966	–	–
Specific collector area, ft^3/1,000 acfm	811	513	–	–
Gross cloth area, ft^2	–	–	956,595	683,282
Pressure drop, in. WG	1.0	1.0	4.72	3.73
Liquid-to-gas vol. flow rate ratio, gal/1,000 ft^3	–	–	–	–

Medium Sulfur Illinois No. 6 Coal (Case 2)[b]

Parameter	Cold ESP			
Migration velocity, ft/sec	0.418	0.30	–	–
Collecting plate area, ft^2	307,336	613,733	–	–
Specific collector area, ft^3/1,000 acfm	203	282	–	–
Gross cloth area, ft^2	–	–	885,112	632,223
Pressure drop, in. WG	1.0	1.0	4.72	3.73
Liquid-to-gas vol. flow rate ratio, gal/1,000 ft^3	–	–	–	–

High Sulfur Pennsylvania Coal (Case 3)[c]

Parameter	Cold ESP			
Migration velocity, ft/sec	0.386[d]	0.30	–	–
Collecting plate area, ft^2	428,971	789,979	–	–
Specific collector area, ft^3/1,000 acfm	275	354	–	–
Gross cloth area, ft^2	–	–	909,328	649,250
Pressure drop, in. WG	1.0	1.0	4.72	3.73
Liquid-to-gas vol. flow rate ratio, gal/1,000 ft^3	–	–	–	–

[a]Required particulate collection efficiency per the proposed NSPS of 0.03 lb/10^6 Btu: 99.5%.

[b]Required particulate collection efficiency per the proposed NSPS of 0.03 lb/10^6 Btu: 99.4%.

[c]Required particulate collection efficiency per the proposed NSPS of 0.03 lb/10^6 Btu: 99.8%.

[d]Migration velocity is lower than for medium sulfur case due to the high ash content of coal.

Table 4. Particulate Control Cost Analysis

Control Device	Total Installed Cost[a] (1978 dollars)	Total Installed Cost[a] and Inst. Elec. Capacity Charge (1978 dollars)	Aggregate Cost of Ownership and Operation Over 30 Years (1978 dollars)	Total Annualized Cost of Operation[b] 1978 dollars	Mills/kWh[c]	Annual Cos Operatio and Mainten 1978 dollars	Mi
			Low Sulfur Montana Rosebud Coal (Case 1)				
Cold-side ESP	18,633,567	19,209,238	72,947,000	6,604,946	1.7755	220,642	
Hot-side ESP	11,214,934	12,623,368	60,038,000	4,416,378	1.1872	423,124	
Reverse flow baghouse	15,605,788	17,969,442	141,987,000	7,921,770	2.1295	1,397,052	
Collapse + shake bag-house	14,645,403	16,718,784	126,029,000	7,033,680	1.8908	983,507	
Scrubber	19,504,958	27,334,137	224,268,000	10,251,220	2.7557	2,848,311	
			Medium Sulfur Illinois No. 6 Coal (Case 2)				
Cold-side ESP	5,289,612	5,382,821	27,041,000	2,061,167	0.5541	202,048	
Hot-side ESP	8,725,309	9,810,970	53,519,000	3.607,477	0.9698	536,183	
Reverse flow baghouse	15,085,623	17,131,695	134,721,000	7,620,659	2.0486	1,544,013	
Collapse + shake bag-house	14,184,497	15,961,988	118,408,000	6,749,633	1.8144	1,101,698	
Scrubber	19,653,669	25,246,368	245,204,000	10,703,545	2.8773	3,715,188	
			High Sulfur Pennsylvania Coal (Case 3)				
Cold-side ESP	7,268,919	8,108,135	35,649,000	2,798,796	0.7524	261,617	
Hot-side ESP	11,252,677	12,695,721	65,872,000	4,587,859	1.2333	644,957	
Reverse flow baghouse	15,808,259	19,473,208	139,772,000	8,065,957	2.1683	1,616,646	
Collapse + shake baghouse	14,877,822	18,266,841	123,377,000	7,175,971	1.9290	1,163,349	
Scrubber	21,167,265	34,944,548	333,900,000	14,284,449	3.8399	5,965,479	

[a]Installed cost includes equipment and installation costs of the control device and associated ash handling equip
liquor pumps, etc., and the land cost.

[b]Total annualized cost equals the total of all the power costs associated with the operation of the control devic
operating labor, heat loss/cost of reheat, materials cost (lime and makeup water for scrubber), maintenance cost
and all the financial charges including depreciation, taxes, etc. For baghouses, maintenance excludes bag replac
ment since it does not occur every year, but it is considered in the aggregate cost of ownership and operation
(Column 3).

[c]Same as b, expressed in mills/kWh, assuming 500-MWe total capacity and 7,440 operating hours per year.

[d]Same as b but excludes financial charges.

[e]Same as d, expressed in mills/kWh, assuming 500-MWe total capacity and 7,440 operating hours per year.

Table 5. Energy ...

Control Device	Electrical Power (MWe)	Electrical Power Equivalent of Heat Energy Usage (MWe)	Total Annual Energy Cost (1978 dollars)[c]	Total Pow... as P... Plant...
Low Sulfur Montana Rosebud Coal (Case 1)				
Cold-side ESP	0.4121	0.0000	59,486	
Hot-side ESP	1.3374	1.1568[a]	325,628	
Reverse flow baghouse	1.6183	0.0000	233,581	
Collapse + shake baghouse	1.2698	0.0000	183,285	
Scrubber	8.6721	13.2957[b]	2,161,362	
Medium Sulfur Illinois No. 6 Coal (Case 2)				
Cold-side ESP	0.4604	0.0000	157,557	
Hot-side ESP	1.0075	1.0704[a]	467,501	
Reverse flow baghouse	1.4844	0.0000	508,011	
Collapse + shake baghouse	1.1619	0.0000	397,665	
Scrubber	6.1950	12.3022[b]	2,961,870	
Sulfur Pennsylvania Coal (Case 3)				
Cold-side ESP	0.5980	0.0000	205,116	
Hot-side ESP	1.2690	1.0997[a]	561,267	
Reverse flow baghouse	1.6692	0.0000	572,523	
Collapse + shake baghouse	1.3380	0.0000	458,911	
Scrubber	15.2598	12.6388[b]	6,098,600	

[a] In converting the heat loss across hot ESP to an electrical power equivalent, a conversi...
efficiency of 38.8% (same as the default value for the plant overall thermal efficiency)...

[b] In converting the stack gas reheat requirement for a scrubber to an electrical power equ...
it is assumed that steam is used for reheat and the efficiency of a steam-electric turbi...

[c] In computing the total energy cost, the local power cost is used for the electrical powe...
and for the heat energy portion an energy cost of $1.75/10^6$ Btu is assumed.

The model development described briefly in this paper resulted in numerous mathematical equations, but they are easily solvable with a hand calculator. A computer program has also been prepared as part of the work done for DOE on this project. The program is an aggregate of the individual models and thus provides for easy application of the models to any given situation.

As illustrated in the case study analysis, use of the models provides a means of comparing control device options based on any or all of the following cost criteria:

- Installed cost,
- Total annualized cost, $/year or mills/kwh,
- Operating cost, $/year or mills/kwh, and
- Aggregate cost of ownership and operation over lifetime.

Further, control device comparisons can be made based on energy consumption expressed as:

- Electrical power required, MWe,
- Electrical power equivalent of heat,
- Total power as a percentage of plant capacity, and
- Annual cost of energy.

The above comparison of energy and economic impacts of various control options provides a valuable means for selecting the optimum method of control for any given system specifications, including power plant size, coal characteristics, and emission limits.

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1. INTRODUCTION

An important characteristic of most Western coals is that they contain
significantly less sulfur than the 2 to 3 pct sulfur content typical of
coals in the Interior and Eastern coal regions. The sulfur content of
Western coals averages about 0.7 pct, and an average sulfur dioxide removal
efficiency of only 30 to 40 pct is required to meet the Federal standard of
1.2 lb SO_2/MM Btu. At the present time, lime or limestone wet scrubbers are
the most commonly used methods for power plant sulfur dioxide emission
control. Industrial acceptance of this technology has been slow due to
large capital investment requirements, poor operation reliability, and
problems associated with sludge disposal. The majority of the lime and
limestone systems are located on utility boilers burning high-sulfur Interior
and Eastern Province coals. In the West, however, where coal deposits
contain significantly less sulfur, several innovative flue gas desulfuriza-
tion (FGD) techniques are being developed.

One innovative FGD technique developed by the Grand Forks Energy Tech-
nology Center (GFETC) is the utilization of alkali in Western coal fly ash
in a wet scrubber in lieu of lime or limestone. Studies at GFETC (1) have
shown that sufficient amounts of alkali metals, such as calcium, can be
leached from fly ash to provide a means of controlling sulfur dioxide
emissions from utility boilers burning Western coals. At present there are
nearly 2600 MW of generating capacity controlling sulfur dioxide emissions
using fly ash alkali. Additionally, approximately 4200 MW of generating
capacity are currently under construction or being designed which will
utilize the fly ash alkali (FAA) system. These figures include only scrub-
bers designed for sulfur dioxide control, and not those scrubber systems
designed for particulate control on Western boilers, and in which some
sulfur dioxide removal occurs. The utilization of Western fly ash alkali
has had a significant impact on FGD technology.

A more recent trend in the West has been the use of spray dryers for
sulfur dioxide control. This FGD process is based on injecting a concen-
trated slurry of alkali into the flue gas and atomizing the slurry to promote
mass transfer of the sulfur dioxide into the absorbent droplets. The flue
gas is maintained above dew point temperatures, thus eliminating reheat
requirements. The alkali reagent ends up as a fine particulate and is
collected, along with the fly ash particulate, by a fabric filter or an
electrostatic precipitator (ESP). The spray dryer FGD concept appears to be
suitable for power plants burning Western coals, and at least one Western
utility with a new 450-MW plant will employ this concept for sulfur dioxide
control.

arid Western regions where water is scarce. In these semi-arid regions, however, it would be more desirable to have a true "dry" process in which water is required. Additionally, dry methods of FGD would be attractive to utilities requiring a retrofit installation. This type of dry process has been under investigation at GFETC since 1975. The materials investigated to date are nahcolite and trona. The application of these materials involves direct injection into the flue gas duct, followed by collection of the spent sulfur capture agent, along with coal fly ash, using a baghouse or electrostatic precipitator. Thus, there would be no complex chemical equipment to operate, nor flue gas reheat or water requirements, and capital equipment expenditures would be minimal.

The present paper presents a summary of past and present results obtained on a 5000-acfm (saturated) and a 130-scfm pilot plant wet scrubber, laboratory kinetic studies on dry adsorption of sulfur dioxide using nahcolite and trona, and pilot plant results on dry adsorption of sulfur dioxide by duct injection of nahcolite and trona followed by baghouse and ESP collection.

2. ASH ALKALI FGD

An important characteristic of most Western coal ashes is their high alkali content. In general, the alkali content tends to be highest in the lignites, and progressively less prevalent in the subbituminous and bituminous coals. As with Western coal ash content, the ash alkali content can vary widely, ranging from under 10 pct to over 50 pct, with significant variations from mine to mine, and even between locations within a single mine. Studies on the utilization of Western coal fly ash alkali in a wet scrubber were pioneered at GFETC using a 130-scfm pilot plant scrubber and more recently, on a 5000-acfm pilot plant scrubber operating on a side-stream of flue gas from a 238-MW cyclone-fired boiler.

Laboratory Studies

Laboratory studies at GFETC have shown that the fly ash alkali can be solubilized into an aqueous media, and that solubilization is primarily a function of pH. Figure 1 illustrates the calcium oxide availability as a function of pH for three North Dakota lignite fly ashes. The data were generated using batch leach procedures (1) and, in general, indicate an increase in the amount of calcium oxide as the solution pH decreases. Similar trends are evident for most Western coal fly ashes. There are, however, differences in fly ash leach characteristics from different mines and power plants. The calcium oxide content of the three fly ashes shown in figure 1 are nearly identical; however, the percentage of available calcium at pH 7 varies from about 10 pct to about 40 pct. As the solution pH decreases, however, the differences in solubilities become less significant and tend to approach similar values. The variations in alkali solubilities can be attributed to differences in chemical composition of the original coal, and also to differences in the boilers from which the fly ash was derived. The alkali solubility data do indicate that significant amounts of calcium alkali can be leached from the fly ash for use in a wet scrubber to control sulfur dioxide emissions.
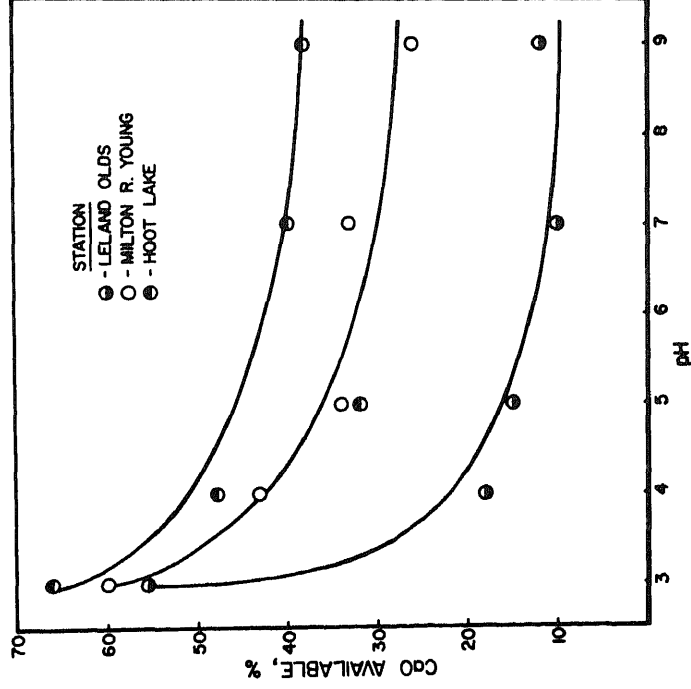
Figure 2. – Flow diagram of 130-scfm pilot plant scrubber, Grand Forks Energy Technology Center.

Figure 1. – Effect of pH on calcium oxide availability for three Western lignite fly ashes.

alkali to sulfur ... the amount of ...
ash alkali that would be available for use in a wet scrubber would depend
the coal ash content, method of firing (pc versus cyclone), and scrubber
operating conditions (liquor pH values); however, there is often ample f
ash alkali available to react with sulfur dioxide in a wet scrubber.

Pilot Plant Studies

Tests at GFETC have been conducted using a 130-scfm pilot plant scru
ber, shown in figure 2, and a 5000-acfm pilot plant scrubber at Center,
North Dakota, shown in figure 3. Objectives of tests using the 130-scfm
pilot scrubber have been to determine sulfur dioxide removal efficiencies
calcium sulfate saturation levels and scaling rates as a function of sta
gas sulfur dioxide concentrations, fly ash add rate and alkali content,
supplementary alkali requirements, levels of recirculated suspended soli
liquid-to-gas ratios, amount of makeup water, and total dissolved solids
(2,3,4).

The 5000-acfm pilot scrubber was used to conduct a test program und
a cooperative agreement among Combustion Equipment Associates (CEA), Art
D. Little Company (ADL), Minnkota Power Cooperative (MPC), Square Butte
Electric Cooperative (SBEC), Minnesota Power and Light Company (MP&L), a
GFETC. The four major objectives of the cooperative program were: 1) T
generate design criteria and determine operating conditions for a 450-MW
scrubber using only fly ash alkali; 2) To conduct a parametric study at
operating conditions representative of steady state using fly ash in amo
typically available from both cyclone- and pc-fired boilers; 3) To inves
gate low pH scrubbing to increase utilization of the fly ash alkali; and
To investigate the effects of high sodium and magnesium concentrations o
ash alkali utilization and sulfur dioxide removal efficiencies at low li
to-gas ratios (5,6,7,8).

The current test program on the 130-scfm pilot scrubber duplicated
parameters investigated on the 5000-acfm pilot scrubber. The objectives
the tests were to characterize sulfur dioxide removal efficiency, calciu
oxide utilization, rate of scale formation, calcium sulfate saturation,
slurry retention time, and level of recirculated suspended solids on the
scfm pilot scrubber. This paper will compare selected results obtained
the 130-scfm pilot plant to results obtained on the 5000-acfm pilot plan

Figure 4 illustrates the sulfur dioxide removal efficiency and calc
oxide utilization as a function of stoichiometric ratio. The inlet sulf
dioxide and liquid-to-gas (L/G) ratio were maintained at nominal values
1000 ppm (dry) and 60, respectively. The level of suspended solids vari
from about 0.5 pct to about 12 pct. The averaged data obtained on the 5
acfm pilot scrubber (6) are represented by the solid curve for sulfur
dioxide removal, and the dashed line for calcium oxide utilization. The
squares represent sulfur dioxide removal efficiency, and the circles rep
sent the corresponding calcium oxide utilization obtained on the 130-scf

Figure 3. - Flow diagram of the 5000-acfm (saturated) pilot plant scrubber, Square Butte Electric Cooperative, Center, N. Dak.

Figure 4. - Sulfur dioxide removal and fly ash CaO utilization as a function of stoichiometric ratio at 1000 ppm SO_2 and a L/G of 60 gal/1000 acf. Data obtained from the 5000-acfm pilot plant scrubber are denoted by the dashed and solid lines. Data obtained from the 130-scfm pilot plant scrubber are denoted by circles and squares.

using other Western fly ashes in the 130-scfm pilot plant scrubber.
Eventually, data from the 450-MW scrubber at operating conditions simil
pilot plant conditions will be obtained, and will provide a means of pr
jecting pilot plant results to a full-scale scrubber using any reagent.

The degree of calcium sulfate saturation is related to scaling pro
in a Western scrubber. Control of scaling must be approached different
for low-sulfur Western coals than for Eastern coals, primarily due to t
high state of sulfur oxidation. Control of scale formation in the fly
alkali system will depend most directly on maintaining a relatively co
pH, and on circulating a sufficiently high level of suspended solids, a
allowing sufficient time and mixing to desaturate calcium sulfate in th
solution. The recirculated suspended solids are composed of calcium su
and undissolved fly ash particles, which can assist in maintaining the
a constant value. If the sulfur dioxide levels should significantly
increase, the undissolved fly ash suspended solids react with the exces
and effectively dampen large pH fluctuations.

The effects of suspended solids and retention time on calcium sul
saturation on the 130-scfm pilot plant scrubber are not clearly define
data using suspended solids ranging from 0.5 pct up to 11.5 pct indicat
effect on saturation, remaining approximately constant at about 200 pct
These results do not agree with results obtained on the 5000-acfm scrub
which indicate a decrease in saturation values in the suspended solids
of 1 to 6 pct, and no effect from 6 pct up to about 12 pct. The satura
values were calculated using activity coefficients. Data generated by
liquor retention times from 4 minutes to 16 minutes also indicate no ef
on calcium sulfate saturation, and the values were generally constant a
about 200 pct. However, scale formation was not detected during experi
on either the 130-scfm pilot plant scrubber or on the 5000-acfm pilot p
scrubber.

One characteristic of scrubbing with fly ash alkali is the high le
dissolved solids, specifically magnesium, sodium, and sulfate. The su
levels, which represent 99 pct of the soluble sulfur forms in the scrub
liquors from the 130-scfm and 5000-acfm pilot plant scrubbers, may rang
to 8 pct and contribute directly to the high saturation values. The ma
sium and sodium levels are also high, reaching concentration levels up
pct. The overall effect of the high sulfate levels is to increase the
cium sulfate saturation values, with the magnesium and sodium levels
decreasing the saturation values.

A summary of physical characteristics of sludge (8) generated dur
two-week material balance test on the 5000-acfm pilot plant scrubber (
shown in Table 1.

Permeability........................cm/sec..	2.0 x 10^{-6} to 6.5 x 10^{-6}
Porosity....................................	0.64 to 0.77
Moisture..............................pct..	23 to 38
Unconfined compressive strength.......kg/cm^2..	1.0 to 2.5

1/ Range of values for ten samples.

Since the predominant sulfur form in the scrubber liquor is sulfate, t
sludge material is enriched in calcium sulfate in addition to unreacted fly
ash. Therefore, the resulting sludge has excellent settling characteristic
and is readily dewatered. Pozzolanic activity due to unreacted fly ash car
be visually observed, and is also demonstrated by the relatively large valu
of unconfined compressive strength shown in Table 1. The permeability
coefficient for the sludge material ranged from 2 x 10^{-6} cm/sec to 6.5 x 10
cm/sec. These values are one to two orders of magnitude less than lime/lim
stone sludge materials and should pose less of a threat to the environment
when disposed in a landfill.

3. DRY ADSORPTION OF SULFUR DIOXIDE

Many utilities in the West are located in areas where water supplies a
scarce. A true "dry" sulfur dioxide removal system would be an attractive
alternative to a wet scrubber system. Additional advantages of a dry FGD
system are: 1) no complex chemical plant to operate; 2) high reliability;
3) immediate response to fluctuation in sulfur dioxide levels; 4) disposal
a dry waste material; 5) less capital investment requirements; 6) lower ope
ating expenses; and 7) more readily adaptable to retrofit situations. The
FGD technology may be more suitable for utilities burning Western coals sir
the low sulfur content would require smaller quantities of sorbent material
to meet the existing NSPS of 1.2 lb SO_2/MM Btu, or the proposed standard of
85 pct removal.

The objectives of the GFETC dry adsorption program are to determine th
suitability of various materials as dry adsorbents, and to conduct larger
scale parametric tests on promising adsorbents. Two promising materials ar
nahcolite and trona, which are naturally-occurring mixtures of sodium car-
bonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$). This report presents
selected results on kinetic studies using laboratory batch-type fixed-bed
reactors, and on pilot plant tests using a 75-lb/hr pulverized coal-fired
furnace with either a baghouse or an ESP for particulate control.

precise temperature control (10). A schematic of the apparatus is shown
figure 5. Simulated flue gas of the desired composition was passed throu
the reactor containing a thin bed of adsorbent.

When nahcolite and trona are exposed to elevated temperatures, sodiu
bicarbonate is converted to sodium carbonate, resulting in a significant
change in the specific surface area. The bicarbonate-to-carbonate conver
sion product is commonly said to be activated. Figures 6 and 7 illustrat
effects of temperature and time on surface area for nahcolite and trona,
respectively. For both adsorbents, the maximum specific surface area was
achieved at about 600° F. At temperatures above 600° F, the specific sur
area decreased significantly due to sintering of the particle surface. T
sintering effect was verified by SEM photographs (10). The data indicate
that the bicarbonate-to-carbonate conversion occurs more rapidly for nahc
(see fig. 6) than for trona (see fig. 7), especially at temperatures abov
500° F. Additionally, nahcolite has a higher specific surface area than
over all temperature ranges. In the present experiments, both adsorbents
preheated at 600° F for two hours to ensure an equivalent starting mater
for all test conditions. Future plans include redesigning the reactor sy
to allow charging the adsorbents directly into the preheated batch react
with gas flow established.

Figure 8 illustrates the effect of temperature on sulfur dioxide ads
tion using nahcolite. In general, the sulfur dioxide adsorption profiles
indicate an initial rapid increase which levels off to a relatively cons
value for the time range investigated. For the time range of zero to 10
seconds, the adsorption rate increases with temperature up to about 650°
However, the data collected at 750° F indicate a slight reduction in adsc
tion. The decreased adsorption at 750° F may be attributed to sintering
the particle surface, causing a decrease in specific surface area.

Figure 9 illustrates the effect of particle size on sulfur dioxide
adsorbence using nahcolite. The results indicate that as the particle s
decreases from an average particle diameter ($\overline{D}p$) of 0.5 mm to 0.09 mm, t
amount of sulfur dioxide adsorbed was doubled. The adsorbent utilization
the 0.09 mm particles was about 98 pct after 200 seconds. An examination
the reacted nahcolite using SEM techniques indicated that the lower adso
tion of the larger particles was due to pore blockage by an ash layer of
sodium sulfate. For both the 0.5 mm and 0.19 mm reacted particles, the
investigation indicates a sodium sulfate ash layer penetration of about
mm. These results indicate that an optimum particle size exists, below
which additional adsorbent size reduction is not beneficial. The optimu
adsorbent size would depend on the specific application, gas-solid conta
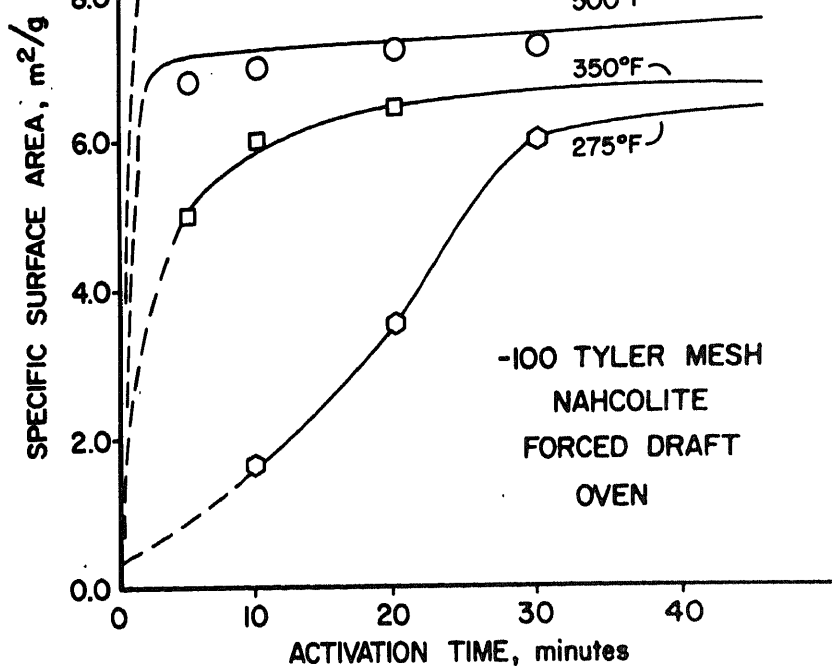temperature, and residence times.
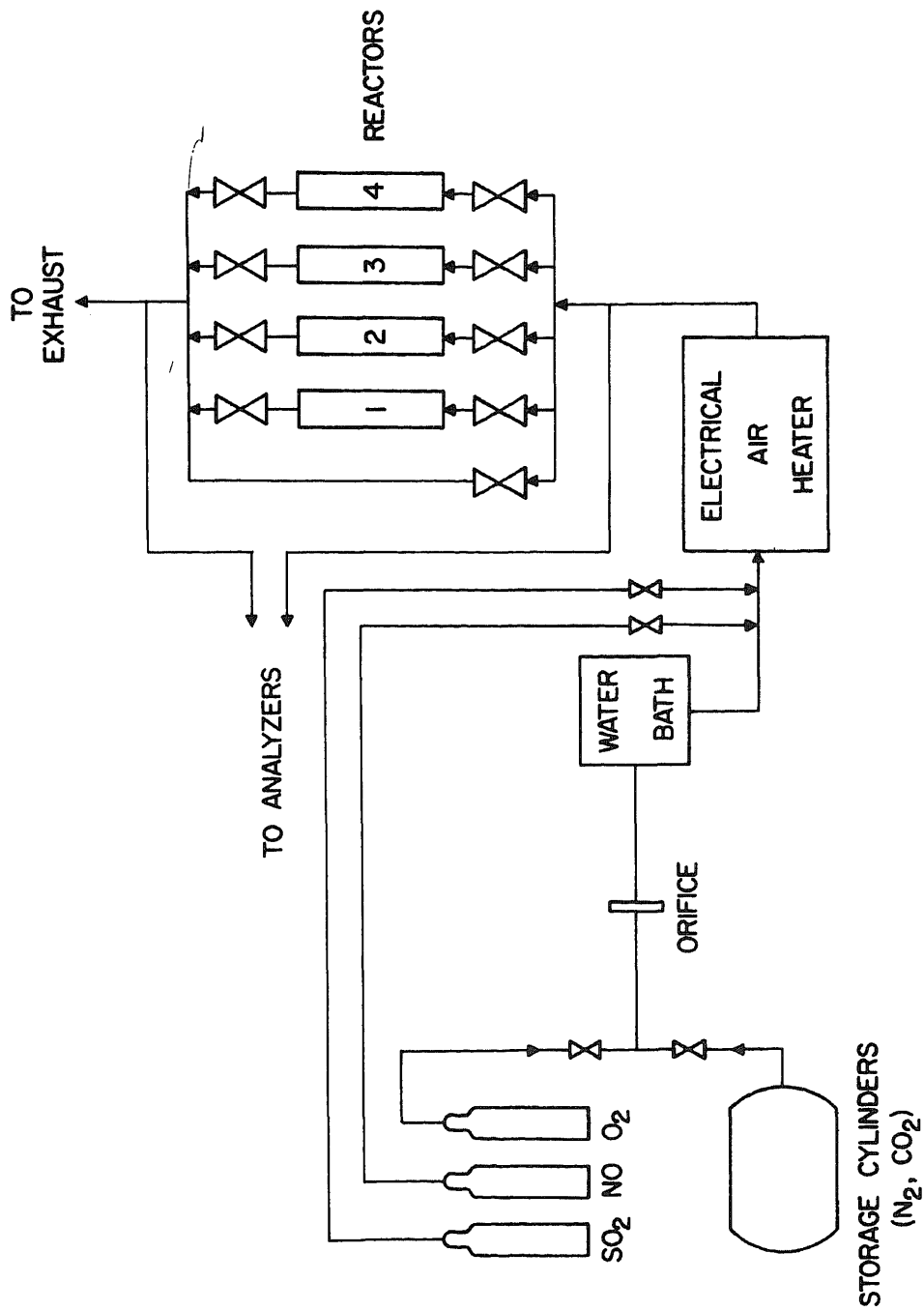
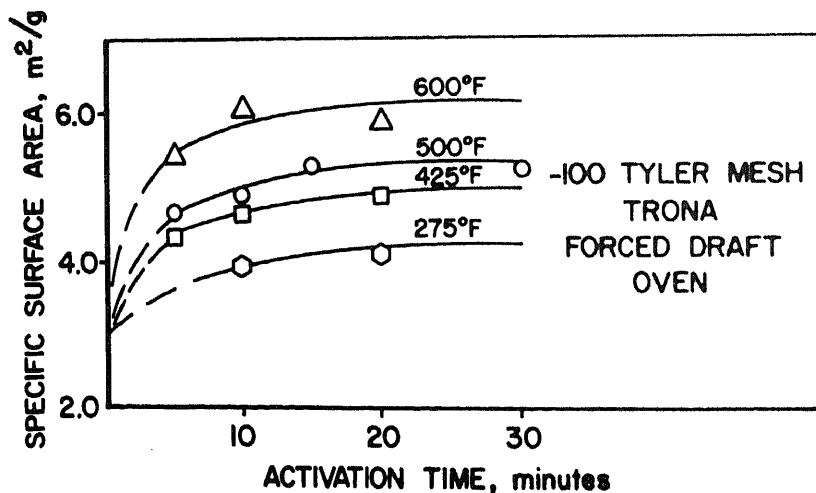Figure 6. - Effect of temperature and time on specific surface area for nahcolite.

Figure 7. - Effect of temperature and time on specific surface area for trona.
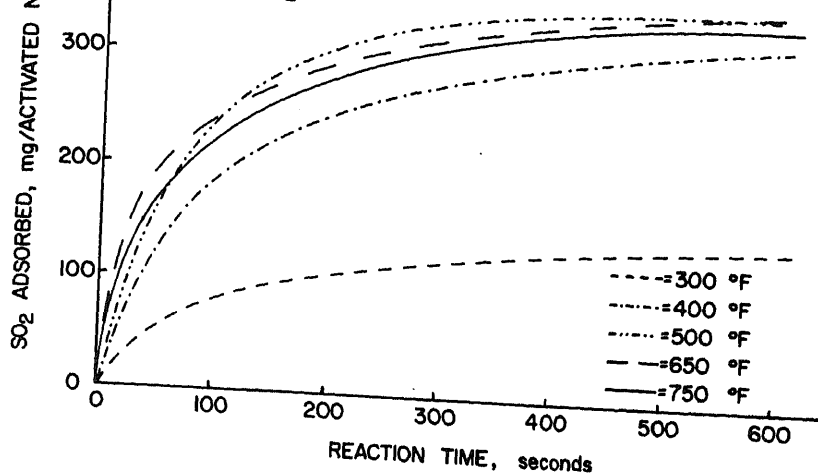
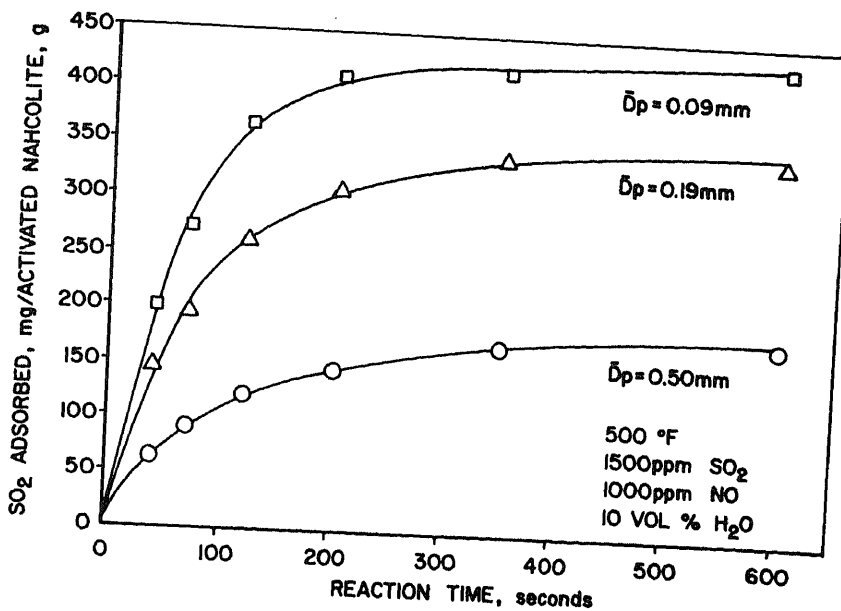Figure 8. - Temperature effect on nahcolite sulfur dioxide adsorbance.

Figure 9. - Effect of nahcolite particle size on sulfur dioxide adsorbance.

increase.

Figure 12 illustrates the sulfur dioxide adsorbence using both n
and trona at identical experimental conditions. The data indicate a
adsorbence for trona compared to nahcolite at each condition investig
Their results may be attributed to the lower specific surface area of
(see fig. 7). However, the differences may be less significant in pr
applications where lower temperatures or longer retention times are e
tered, or smaller trona particles are utilized.

Analyses of reacted nahcolite and trona obtained from the above
for nitrites and nitrates indicate little nitric oxide adsorption. H
when tests with nahcolite were repeated without sulfur dioxide in the
gas, appreciable amounts of nitric oxide were adsorbed, as shown in f
The dashed line represents nitric oxide adsorption in the absence of
dioxide. The solid line represents nitric oxide adsorption in the pr
of 1500 ppm sulfur dioxide. The data indicate significant nitric oxi
adsorption in the absence of sulfur dioxide, and the adsorbent utiliz
approaches 97 pct for a reaction time of 5400 seconds (90 minutes).
results indicate a competitive reaction between sulfur dioxide and ni
oxide for the active sites of the nahcolite adsorbent, with the sulfu
dioxide dominating the reaction kinetics. Preliminary data indicate
greater amounts of nitric oxides are adsorbed at 300° F than at highe
peratures. This apparent decrease in adsorption may be due to therma
instability of the reaction product; however, additional studies are
Both nitric oxide and nitrogen dioxide adsorption will be investigate
greater detail in future work.

Pilot Plant Studies

Tests have been performed utilizing the GFETC 75-lb/hr, pc-fired
pilot ESP facility, shown schematically in figure 14. The subbitumin
burned in this study was provided by Utah Power and Light (UP&L) from
Kemmerer Mine at Kemmerer, Wyoming. UP&L also provided the nahcolite
obtaining them from the Superior Oil Company.

The pilot plant program was designed to study dry sulfur dioxide
tion as a function of adsorbent material, injection temperature, resi
time, stoichiometric ratio, adsorbent particle size, and collection d
operating temperature under simulated power plant conditions. Flue g
sulfur dioxide removal could occur in any one of three regions in suc
application: 1) during sorbent suspension in the flue gas, 2) during
tion in an electrostatic precipitator, and 3) during collection in a
filter (baghouse). The sulfur dioxide concentrations were maintained
range of 850 to 1000 ppm, approximating the combustion of Kemmerer co
a one pct as-received sulfur content. The present results represent
mary of the work completed to date.

150

SO₂ ADSORBED, mg/... (partial, top of page)

1000ppm NO

□ - 15 VOL % H₂O
△ - 10 VOL % H₂O
O - 5 VOL % H₂O
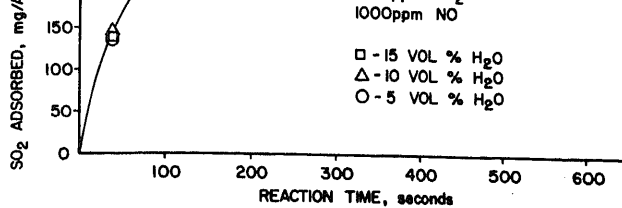
Figure 10. - Effect of flue gas mois-
ture on nahcolite sul...
dioxide adsorbance.
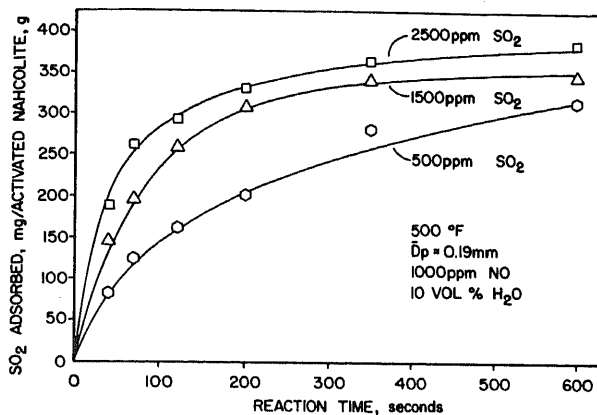
Figure 11. - Nahcolite adsorption a...
various sulfur dioxid...
concentrations.

Figure labels (Figure 11):
2500ppm SO₂
1500ppm SO₂
500ppm SO₂

500 °F
D̄p = 0.19mm
1000ppm NO
10 VOL % H₂O
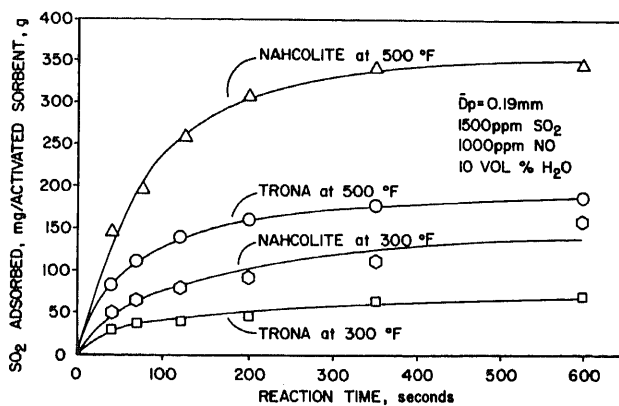
Figure 12. - Comparison of nahcoli...
and trona sulfur diox...
adsorption at two
temperatures.

Figure labels (Figure 12):
NAHCOLITE at 500 °F
TRONA at 500 °F
NAHCOLITE at 300 °F
TRONA at 300 °F

D̄p = 0.19mm
1500ppm SO₂
1000ppm NO
10 VOL % H₂O
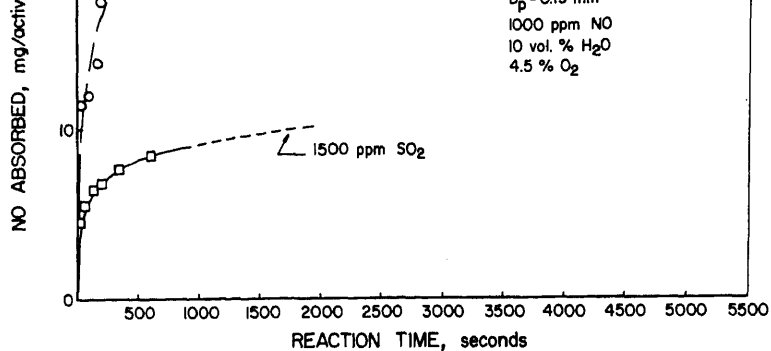
Figure 13. - Nitric oxide adsorbance using nahcolite with and without sulfur dioxide.
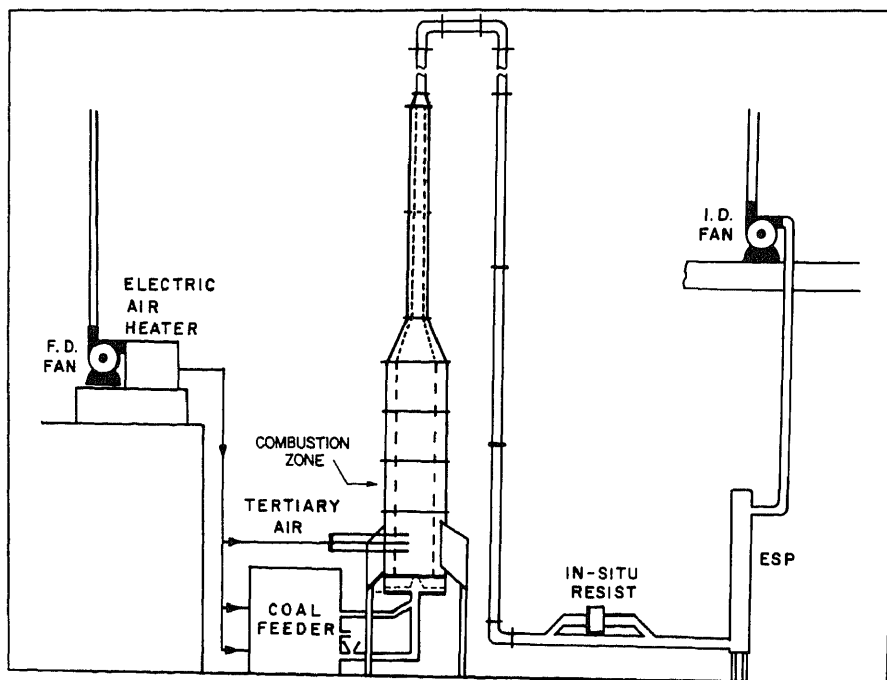
Figure 14. - Schematic of 75-lb/hr pc-fired pilot plant combustor at GFETC.

Tests studying the injection of trona and nahcolite along with the coal into the furnace burner were performed in two ways. In the first case, the makeup sulfur dioxide (required to increase the normal sulfur dioxide level of approximately 320 ppm to the desired level of 925 ppm) was injected after the combustion gases had been cooled to below 2000° F. In the second case, the makeup sulfur dioxide was injected along with the coal into the burner. Data from these tests are summarized in Table 2. In the first case at stoichiometric ratios of 0.9 to 1.8, sulfur dioxide removals ranged from 21 to 39 pct and overall utilizations were nearly constant at 22 pct. These results would indicate an optimum utilization of about 22 pct regardless of adsorbent material or stoichiometric ratio. From 62 to 100 pct of the overall sulfur dioxide removal occurred in zone A (flue gas above 1400° F). The 39 pct maximum removal observed under case 1 conditions is approximately equivalent to that fraction of the total sulfur dioxide resulting from combustion of the coal (320 ppm out of 925 ppm).

Results obtained under case 2 conditions indicate a range of sulfur dioxide removals from 32 to 99 pct at stoichiometric ratios of 0.8 to 2.6. Virtually all of the removal occurred in zone A. Utilizations averaged 41 pct with, again, very little variation with stoichiometric ratio or adsorbent material. These results indicate that nearly all of the sulfur dioxide removal occurs at temperatures above 2000° F when the adsorbents are injected into the flame region. The events occurring in such a process most likely correspond to those postulated for the action of sodium in promoting ash fouling of heat exchange tubes in coal-fired boilers (11). The sodium material volatilizes in the coal flame, forming a reactive vapor which combines rapidly with gaseous sulfur dioxide or sulfur trioxide to form a fine sodium sulfate particulate when cooled. Burner injection of sodium materials for sulfur dioxide control could not be recommended due to the near certainty that severe ash fouling would result in the boiler superheat and reheat sections. To evaluate the potential ash fouling problem, an experiment using nahcolite injected into the burner was conducted using the 75-lb/hr, pc-fired ash fouling furnace at GFETC. The result was formation of a molten, glassy, flowing slag on the simulated secondary superheat tubes. This most assuredly would be an impossible condition in a full-scale boiler.

Adsorption in Flue Gas Suspension

Tests to evaluate the sulfur dioxide adsorbence of nahcolite and trona in a flue gas stream, with injection temperatures ranging from 360 to 1515° F, indicate an optimum injection temperature of about 650° F for both materials. The existence of an optimum injection temperature is in agreement with the results obtained in the laboratory kinetic study (see figures 6, 7, and 8). The data obtained at 650° F are presented in Table 3.

TABLE 2. - Sulfur dioxide adsorption results with adsorbent injected into the flam[...]

Adsorbent Material	Stoich-iometric Ratio	Zone A Flue Gas Prior to 1400° F			Zone B Zone A + Flue Gas Prior to ESP			Zone[...] Zone A +	
		Residence time, sec.	Removal, pct	Utili-zation, pct	Residence time, sec.	Removal, pct	Utili-zation, pct	Residence time, sec.	Rem... p[...]
CASE 1: [1]									
Nahcolite	0.92	3.1	17.7	19.3	4.0	19.9	21.7	5.0	21
Nahcolite	1.00	3.0	13.2	13.2	3.9	16.5	16.5	4.9	27
Nahcolite	1.83	2.9	39.1	21.4	3.7	39.1	21.4	4.6	39
Trona	1.18	2.9	22.1	18.6	3.7	24.6	20.7	4.7	26
CASE 2: [2]									
Nahcolite	0.79	3.1	31.6	42.6	5.0	31.6	42.6	6.0	31.
Nahcolite	2.04	3.1	89.4	43.3	4.9	89.4	43.3	6.0	89.
Trona	1.34	3.1	53.4	39.9	5.0	53.4	39.9	6.1	53.
Trona	2.60	3.0	97.5	37.4	4.8	98.3	37.8	5.8	98.

[1] Adsorbent into burner along with coal, makeup sulfur dioxide injected downstream (flue gas below 2000° F).

[2] Adsorbent and makeup sulfur dioxide injected into burner along with coal.

			Time, sec.	Ratio	pct	tion, pct
Nahcolite	100	640	3.1	0.71	24.0	33.9
	100	640	3.1	1.52	48.2	31.8
Nahcolite	200	650	3.5	1.47	45.6	31.0
	200	650	3.2	1.84	61.2	33.3
Trona	100	640	3.1	1.96	33.0	16.7
	100	630	1.2	1.03	25.6	24.8

The data indicate that, although a sulfur dioxide removal greater than 60 pct was achieved in the best case, the low adsorbent utilization values would probably make such a scheme unattractive for economic reasons. As the selected data illustrate, there is not a clearcut difference for in-duct sulfur dioxide removal between the minus 100 and minus 200 mesh nahcolite. As in flame injection, utilization of nahcolite adsorbent was independent of stoichiometric ratio at the conditions studied. There is some indication from the whole body of data obtained that below the residence times available in a power plant, greater than three seconds, and at injection temperatures below the optimum 650° F, the finer material performs somewhat better. At injection temperatures above about 800° F, there is no apparent difference between minus 100 mesh nahcolite and minus 100 mesh trona. At injection temperatures near the optimum and below, the minus 100 mesh nahcolite has a distinct advantage. Although tests have not been run to evaluate a finer trona for duct sulfur dioxide adsorption, the data comparing the two size ranges of nahcolite would lead one to expect somewhat improved performance for a minus 200 mesh trona.

Adsorption in a Pilot Plant ESP

A series of tests were conducted to study the nahcolite and trona adsorbents in systems which include an ESP. The motivation was twofold: 1) to evaluate such a system for sulfur dioxide removal, and 2) to determine the effect of the injection of relatively large quantities of sodium material on ESP operation. During ESP operation, the overall sulfur dioxide removals and adsorbent utilizations were increased an average of 55 pct above that occurring in suspension. It is felt that this apparent improvement due to the presence of the ESP might not be as substantial in a full-scale precipitator. At least two factors would tend to reduce the potential effectiveness of the increased flue gas residence time in a full-scale precipitator. In the first place, the majority of the removal of the input particulate mass in a full-scale ESP occurs in the first few feet, significantly reducing the portion of the apparent long residence time which is effectively adsorbent/flue gas contact time. Secondly, the collection electrode of the pilot ESP utilized

reduction in resistivity from 10^{12} to 10^9 ohm-cm. Due to the reduction in resistivity, there was virtually no change in ESP mass removal efficiency. The doubling or tripling of the inlet particulate concentration, however, resulted in a twofold increase in the outlet particulate concentrations in all cases studied.

Adsorption in a Pilot Plant Baghouse

A series of tests were conducted to study the nahcolite and trona adsorbents in systems which include a baghouse. The pilot baghouse was substituted for the pilot ESP in the system illustrated in figure 14. Test with nahcolite indicate that utilization in the baghouse was independent of adsorbent size below 100 mesh, injection temperature, and stoichiometric ratio at baghouse cycles of 45 to 60 minutes. In these cases, adsorbent injection was maintained at a constant level for the entire cycle. The overall adsorbent utilizations fell in the range from 63 to 77 pct for all cases. More tests are required to evaluate the effect of baghouse operatin temperature.

The particle size of the adsorbent appears to be a significant factor when trona is used as the adsorbent, as shown in figure 15. The utilizatio shown in figure 15 for the minus 200 mesh trona fall within the range deter mined for nahcolite (63 to 77 pct), indicating that properly sized trona ma be as effective as nahcolite when used in conjunction with a bahouse. More tests are required to establish what additional parameters might significar effect trona sulfur dioxide adsorption in a baghouse.

Figure 16 illustrates an interesting aspect in the development of dry sulfur dioxide adsorption techniques utilizing a baghouse. In this case, the trona at an overall stoichiometric ratio of 0.96 was injected during th first 8 minutes of a 74-minute test. A series of such curves over a variet of cycle durations and injection schemes should aid in the development of b optimum dry adsorbent injection methods and baghouse designs for use in suc a sulfur dioxide removal system. Optimization of the system should include evaluation of adsorbent injection techniques and baghouse cycling. In general, dry sulfur dioxide adsorption utilizing nahcolite and trona in con junction with a baghouse appears to have potential as a flue gas desulfuri-zation technique. Continuation of the current test program is certainly warranted. Larger-scale testing to confirm the potential indicated by this work, as well as that of others (12,13) should be planned in the near futur
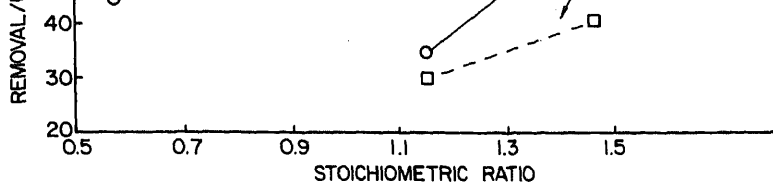
Figure 15. - Adsorbent utilization (denoted by dashed line) and sulfur dioxide removal (denoted by solid line) as a function of stoichiometric ratio using minus 100 and minus 200 mesh trona in a baghouse.
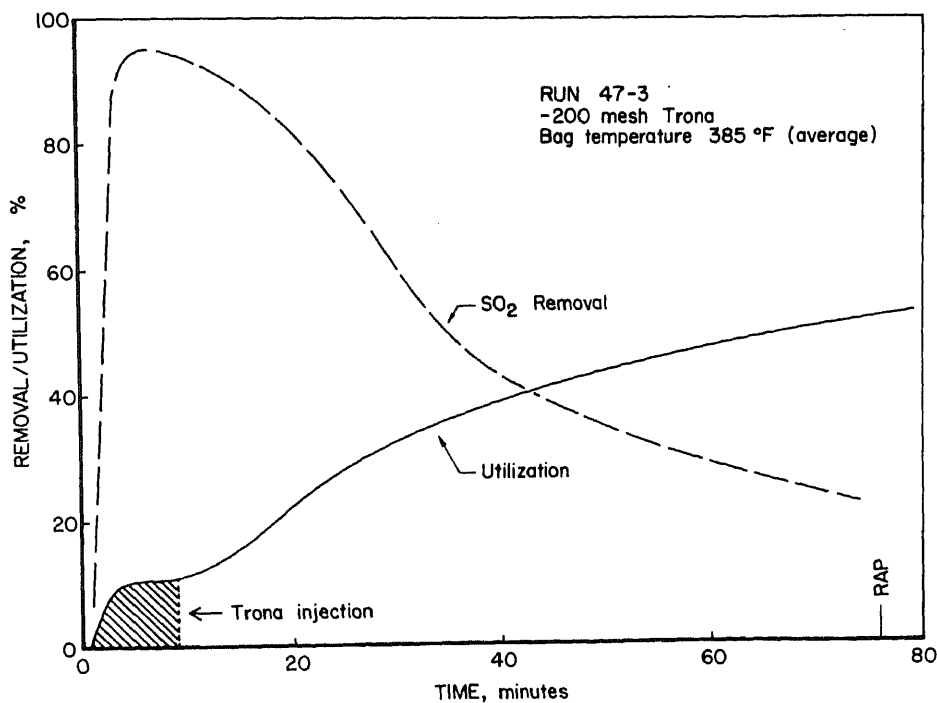
Figure 16. - Sulfur dioxide adsorption results utilizing minus 200 mesh trona with a baghouse and non-continuous adsorbent injection.

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Introduction

The literature on past and current global CO_2 studies yields a perspective on the bounds of the potential atmospheric CO_2 problem. During the last one hundred years or so, the release of fossil carbon as CO_2 has increased at an exponential rate as shown in Figure 1.[1] As a result, the concentration of CO_2 contained in the atmosphere has grown by about 12%, increasing from about 295 ppm by volume in 1960 (pre-industrial revolution) to the current level of 331 ppm. Except for short periods during World Wars I and II and the depression, the release rate of fossil carbon has increased at the rate of about 4.3% per year.[2] At present, with no CO_2 emission controls, about 5×10^9 metric tons of carbon per year as CO_2 are emitted to the atmospher by the burning of fossil fuels from worldwide sources. About 50% of this carbon can be accounted for by the increase in the CO_2 concentration of the atmosphere. The remaining carbon is assumed to be absorbed by the oceans and by the land biota, in unknown proportions. Deforestation considerations and the possibility of the release of CO_2 from the Pacific Ocean waters south of the equator due to the "Southern Oscillation",[3] a naturally occuring phenomenon of unknown cause, tend to becloud the issue. A better understanding of the carbon cycle is definitely needed.

If the use of fossil fuels continued to grow at 4.3% per year until the estimated supplies thereof were exhausted, the use rate at the end of this period would be almost 64 times the current use rate, and the total CO_2 injected into the atmosphere, during this period, would be about 12 times the pre-industrial content of the atmosphere. Obviously, such a use pattern cannot be tolerated; however, based on more realistic assumptions, it is predicted that the concentration of atmospheric CO_2, relative to the pre-industrial value, could increase by a factor of from about 2 (low use case) to about 5 (high use case) during the next one hundred years. The low use case corresponds to a fossil fuel growth rate of 2% per year until the year 2025, followed by a symmetrical decrease as alternative and renewable energy sources become more available and the use of fossil fuels is discouraged. The high use case corresponds to an initial annual growth rate of 4.3% with subsequent reductions in proportion to the ultimate fossil fuel supply that has been consumed. In both cases, about 50% of the emitted fossil carbon is assumed to be taken up by the oceans and land biota.

Of primary concern is the warming ("greenhouse") effect which could be produced by these increased CO_2 concentrations due to the absorption by CO_2 of a portion of the infrared radiation returning to space from the earth [the infrared absorption spectrum of CO_2 shows strong absorption bands at 667 cm^{-1} (15 μ) and 2349 cm^{-1} (4.26 μ)]. Additional effects caused by

mean global temperature rise of from about 1 to 5°K over the next one hund
years and from about 2 to 10°K for the high case. A temperature of 1 or
during this period may be acceptable, however, a rise of 10°K would proba
cause catastrophic effects.
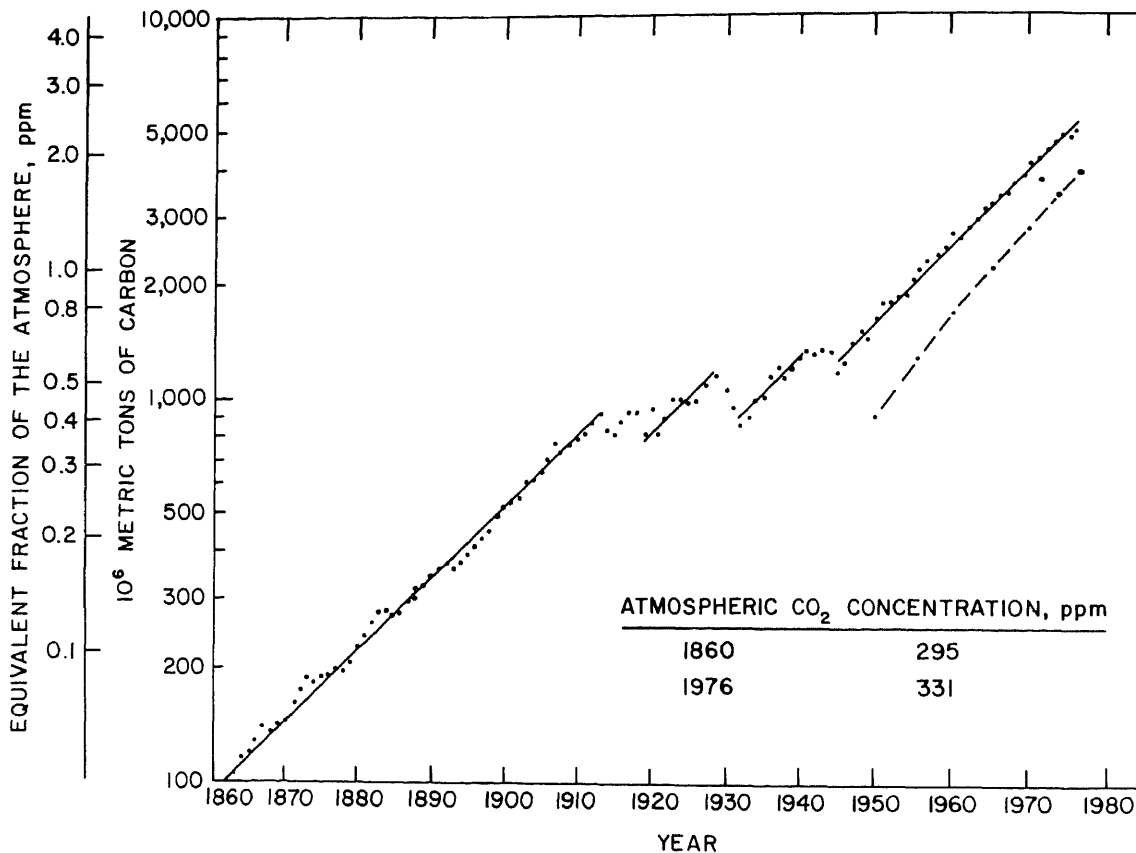
FIGURE 1: CO_2 PRODUCTION FROM FOSSIL FUELS AND CEMENT

——— WORLDWIDE
— — — WORLDWIDE LESS U.S. SOURCES

Increased concentrations of particulate matter (and aerosols) in the
global air mass could produce a cooling effect by backscatter of incoming
solar radiation and thus counteract, to some degree, the warming produced
by increasing CO_2 levels. However, environmental emission regulations on
particulates, as well as on other identified pollutants, have become more
and more stringent during recent years and the trend is expected to contin
Furthermore, to deliberately attempt to counteract the effects of CO_2 by

it may be necessary to limit industrial CO_2 emissions in the future. Up to
the present, there has been practically no concern about the health or
environmental effects of CO_2 discharge; accordingly, there are no regulations
applicable to CO_2 emissions. Options for CO_2 control have received little
attention and although preliminary evaluations indicate that control is
theoretically possible, it may not be technically or economically practicable.
It thus becomes important at this time to examine CO_2 control options to
determine the technical feasibilities and the economic costs, should the need
arise for CO_2 control.

Impact of US Emissions

In order to determine the impact of fossil fuel use in the United States
on overall (worldwide) CO_2 emissions, we have superimposed several points on
Figure 1, based on US fuel use data for the years 1950, 1955, 1960, 1965,
1970, 1973,[5] and 1976.[1] The points were obtained by subtracting the estimated
emissions of carbon (as CO_2) by US sources from the corresponding worldwide
emissions for each of the above years, and thus indicate the quantities of
carbon that would have been emitted if the US had not burned any fossil fuels
during these years. The reduction in carbon (and thus in CO_2) by this hypo-
thetical non-use of fossil fuels in the US ranges from 0.32 ppm in 1950 to
0.64 ppm in 1973 (and in 1976) as given in Table 1. However, during this
period the percentage of the total yearly emissions contributed by the US
decreased from 43% in 1950 to 27% in 1976. This is due to an increasing rate
of fossil fuel usage in developing nations and a decreasing rate in the US.
Furthermore, it is projected that the contributions to global CO_2 production
by the US and Canada will decrease to about 8% by the year 2025. Developing
nations will account for 36% of the CO_2 production, the USSR and Eastern
Europe 27%, Asia 19%, Western Europe 7%, and Japan and Australia 3%.[1] There-
fore, it would appear that a worldwide effort would be required to effectively
control the level of atmospheric CO_2. A unilateral effort by any one nation
probably would not be very effective.

Impact of Coal Utilization

Table 2 contains a source distribution of carbon (CO_2) produced from
major worldwide sources during the years 1970 through 1976.[1] For the year
1976, using the heating values of 18,000 BTU/lb of contained carbon for coal,
22,400 BTU/lb carbon for fuel oil and 31,500 BTU/lb carbon for natural gas,
and assuming that all fossil energy was produced by the burning of solid
coal, the carbon release to the atmosphere would have been roughly 6 x 10^9
metric tons or about 1.2 times the quantity actually emitted. Energy
differences required in mining versus drilling, preparation, transportation,
etc. and in combustion efficiencies were not taken into account. Note that
the weight ratio of CO_2 produced by the burning of coal to that produced by
the burning of natural gas, for the same energy output, is about 1.8 and for
coal versus fuel oil about 1.2. If, in the above calculation, we had assumed
that the natural gas and petroleum consumed in 1976 had been replaced by coal

since 1860.

Table 1

U.S. CONTRIBUTION TO ATMOSPHERIC CO_2 EMISSIONS
COMPARED TO ALL OTHER WORLDWIDE SOURCES[1,5]

Year	Incremental Atmospheric CO_2 Concentration in ppm		% U.S. Contribution	% Others
	Worldwide	U.S.		
1950	0.74	0.32	43	57
1955	0.92	0.36	39	61
1960	1.18	0.39	33	67
1965	1.47	0.46	31	69
1970	2.00	0.58	29	71
1973	2.27	0.64	28	72
1976	2.38	0.64	27	73
2025 Est.			8	92*

*Developing nations estimated to account for 36% of total worldwide emissions.

Impact of Alternative Energy Sources

The expected reduction in the US contribution to worldwide atmosph
CO_2 emissions is partially attributed to the development and implementa
of alternative energy sources, which includes, nuclear (fission and fus
geothermal and solar. The impact of these alternatives in the US depen
to a great extent on four factors: (1) the demand growth for energy in
US, (2) the availability of the technology, (3) the capital and product
costs, and (4) the supply of world petroleum sources and the demand of
developing countries for petroleum and coal resources. Although uncert
in all of these factors make it extremely difficult to estimate the imp
of substitute energy sources, nevertheless some projections can be made

the US in the next 50 to 100 years as listed in Tables 3 and 4. Thus, if the energy demand no more than doubles in the next 50 years, and the fossil fractional use decreases about in half the US would then contribute approximately the same amount as at present to the world atmospheric CO_2 emissions, as indicated by the CO_2 Index in Table 4. However, the other countries would exceed their present contributions as they develop technologically at a higher rate. Eventually even these countries will acquire alternative energy sources and the CO_2 emissions may then become stabilized.

<center>Table 2</center>

<center>WORLD-WIDE CO_2 EMISSIONS BY SOURCE</center>

<center>All entries in 10^6 metric tons carbon as CO_2</center>

Source	1970	1971	1972	1973	1974	1975	1976	1976 Distribution %
Coal	1497	1479	1499	1527	1550	1626	1676	33.2
Lignite	237	239	243	246	246	249	260	5.1
Crude Petroleum & N.G. Liquids	1803	1907	2011	2203	2213	2107	2224	44.1
Natural Gas	545	583	614	646	659	665	675	13.4
Natural Gas Flared	90	94	100	110	113	105	113	2.2
Cement	82	88	93	95	95	100	99	2.0
Total carbon as CO_2	4254	4390	4560	4827	4876	4852	5047	
Incremental atm CO_2 Conc. (ppm)	2.00	2.07	2.15	2.27	2.29	2.28	2.38	
U.S. Emissions Contribution	0.58			0.64			0.64	

In the interim, there is thus sufficient incentives, even when considering alternative energy sources, to systematically examine the technological and engineering factors for controlling CO_2 emissions. The systematic study would be of value for identifying candidate CO_2 control scenarios and to determine their technical and economic practicabilities. The environmental control technology of CO_2 may be of short term value for the US but of much more value in the longer term for worldwide purposes.

Table 3

ANTICIPATED DISTRIBUTION OF ALTERNATE ENERGY SOURCES

FOR THE U.S. IN THE NEXT 50 TO 100 YEARS

	Percent of Demand		
Source	1975	2025	2075
Fossil (coal, oil and gas)	90%	50%	30%
Nuclear (Fusion and Fission)	5	20	30
Solar	0	20	30
Hydro, Geothermal and others	5	10	10
Total	100	100	100

Table 4

U.S. AND WORLD ENERGY GROWTH AND

DISTRIBUTION OF ALTERNATIVE SOURCES

	1975			2025		
Region	Quads	Fraction Fossil	CO_2 Index*	Quads	Fraction Fossil	CO_2 Index
U.S.	75	0.90	67.5	150	0.50	7...
Other Nations	175	1.00	175.0	1100	0.84	9...
World (total)	250	0.97	242.5	1250	0.80	100...

*CO_2 index is product of Quads consumed and fossil fuel fraction.

Logic for Constructing Scenarios for CO_2 Control Technology

The suggested logic for guiding the construction of CO_2 control sc...
is shown in block diagram form in Figure 2.[7] The sequential steps to be
followed are:

1. Control Point Selection – Three potential control points (CO_2 r...
sites) are available for regulating the concentration of CO_2 in the atmo...
sphere: (1) the atmosphere itself, (2) the oceans, and (3) the stacks...

will reflect on the size of operation, the number of required sites, removal efficiency, energy requirements, the comparative economics and on the overall feasiblilty of operation.

Figure 2

LOGIC DIAGRAM FOR THE CONSTRUCTION OF SCENARIOS
FOR CONTROLLING ATMOSPHERIC CARBON DIOXIDE
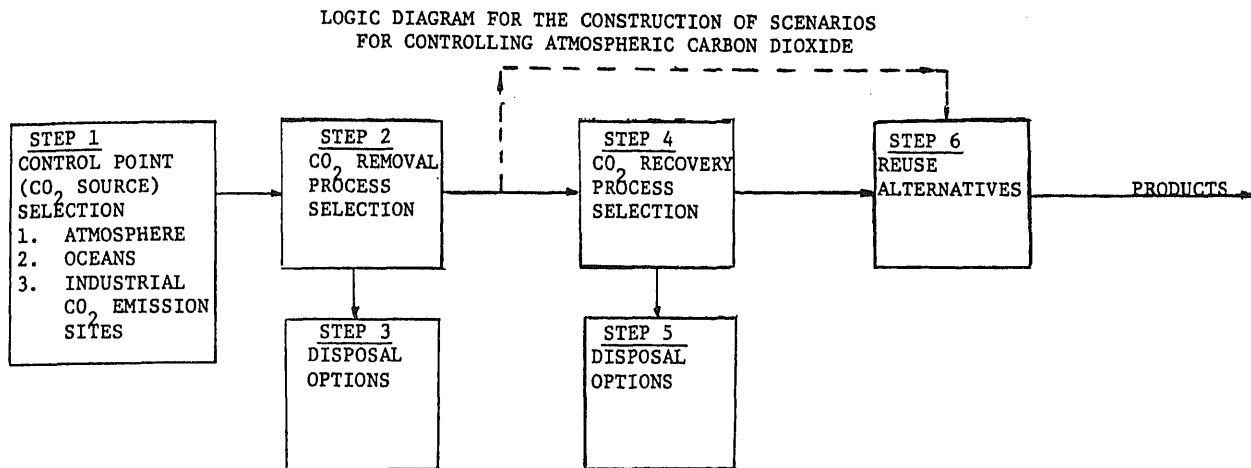
A listing of options for the removal, recovery, disposal, and reuse of CO_2 as a function of control point is contained in Tables 5A through 5E.[7] Use of alternative fuels and energy sources are also considered as a potential means of controlling atmospheric CO_2.

2. Removal Process Selection – Once a control point has been selected, the next task is to survey available removal processes to determine those which appear to be feasible, and compatible, with the selected control point.

3. Identification of Disposal Alternatives for Captured CO_2 – This task involves the identification of alternatives which are available for disposing of the captured CO_2 (Step 2) directly, that is without going through a CO_2 recovery step, (e.g. desorption/sorbent regeneration). For example, if a naturally occurring, inexpensive and non-polluting CO_2 adsorbent was available the spent sorbent containing the captured CO_2 could be buried or stored in abandoned mine shafts rather than reused. A comparison between direct disposal versus CO_2 desorption/sorbent regeneration would be made at the time of scenario evaluation since each alternative would represent a separate scenario. For the case of CO_2 extraction by refrigeration or distillation, no desorption step is required.

4. CO_2 Recovery Process Selection – For a once through system, the quantity of sorbent consumed in absorbing or adsorbing CO_2 would generally be very large because of the vast quantities of CO_2 that would have to be removed from the environment to effectively control the level of atmospheric CO_2. Thus, it may be advantageous, and in fact would be necessary in most cases, to desorb captured CO_2 and regenerate and reuse the sorbent.

and each selected in turn for evaluation.

5. <u>Identification of Disposal Alternatives for Recovered CO_2</u> - This task is similar to that described under Step 3, above, except that CO_2 would be in the form of a relatively pure gas, liquid or solid; that is, appreciable quantities of sorbents would not be present in the effluent (disposal) stream. Note that in the case of CO_2 extraction by refrigeration, liquid or solid CO_2 would be produced directly in the extraction step (Step 2) and therefore Steps 4 and 5 would not be required.

6. <u>Identification of CO_2 Reuse Alternatives</u> - The last step in the process of scenario construction involves exploring and identifying reuse possibilities for recovered CO_2 (Step 4). Several possibilities have been identified in Tables 5A through 5E. One option which has been given some consideration is to catalytically convert the recovered CO_2 to methanol by reaction with hydrogen using a non-carbonaceous energy source.[6] In some cases, it may be possible to proceed directly from CO_2 removal (Step 2) to CO_2 reuse as indicated by the broken line in Figure 2.

Since there are several key considerations in evaluating prospective control scenarios, e.g., energy and equipment requirements and sorbent property and losses, each scenario must be analyzed in some detail before realistic decisions can be made concerning its overall feasibility and comparative merits. A simplified approach could place emphasis on the wrong strategy and lead to false predictions and/or conclusions. However, the prime consideration in evaluating a CO_2 control system which derives its energy from a fossil fuel source is the energy required by the control system. In these cases, additional CO_2 would be generated in supplying energy to the control system and a point could be reached where more CO_2 is generated in supplying energy to the control system than is removed from the control point.

Carbon Dioxide Generation as a Function of Fuel and Energy Source

There is a gradation in the amount of carbon dioxide produced per unit energy released depending on the type of fuel or energy source used. Table 6 lists a number of sources of fuels, the heating values and the unit CO_2 generation in terms of mass of CO_2 generated per unit energy released (lb CO_2/1000 BTU) in utilization of fuel.

It is noted that the least CO_2 generation per unit energy output is produced by natural gas and by hydrogen from reforming of natural gas. The next smallest amount of CO_2 released is from natural petroleum products i.e. oil and gasoline. Further increase in unit CO_2 is given by wood, alcohol, and benzene. This is followed by coal and coke.

CONTROL POINT	CO_2 REMOVAL OPTIONS

I. ATMOSPHERE

Absorption by Liquids
1. Water
2. Sodium carbonate
3. Potassium carbonate
4. Caustic
5. Amines (e.g. monoethanolamine and diethanolamine)
6. Other physical solvents (e.g. methanol and N-methylpyrrolidine)
7. Other chemical solvents (e.g. ammonia and Alkazid)
8. Combined physical and chemical absorbents (e.g. Sulfinol)
9. Physical a/o chemical solvents followed by caustic scrubbing

Adsorption by Solids
1. Naturally occurring sorbents (e.g. natural clays and zeolites)
2. Waste oil shale from retort operations
3. Molecular sieves

Extraction by Refrigeration

Increased Planting of Land Biota – photosynthesis

Absorption by Deep Ocean Waters – process used in conjunction with ocean thermal gradient power cycle.

Dilute Phase Methanation of Atmospheric CO_2 – hydrogen supplied by non-fossil energy source.

II. OCEANS

Strip CO_2 with H_2

Distillation or Steam Stripping

Acidification Followed by Degasification

III. MAJOR INDUSTRIAL CO_2 EMISSION SOURCES (e.g. fossil plant stacks)

Absorption by Liquids – same alternatives as for the atmosphere.

Adsorption by Solids – same alternatives as for the atmosphere.

Extraction by Refrigeration

Advanced Power Cycle – air separation followed by combustion of fossil fuels by oxygen. Recovery of CO_2 from combustion by above processes

Use of Alternative Energy Sources

OPTIONS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE
OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT	OPTIONS FOR DISPOSAL OF CAPTURED CO_2

I. ATMOSPHERE	CO_2 Captured by Liquids
	1. Evaporate water, then bury residue--
	   carbonates and caustic sorbents only
	2. Deep oceans - water only
	
	CO_2 Captured by Solids
	1. Subterranean (e.g. abandoned
	   mine shafts).
	
	CO_2 Captured by Refrigeration
	1. Extraterrestrial
	2. Deep oceans
	3. Antarctic region
	4. Subterranean
	
	CO_2 Captured by Plants
	1. CO_2 remains integral part of plant
	
	CO_2 Captured by Deep Ocean Waters
	1. Deep ocean

II. OCEANS	CO_2 Captured by Distillation 1. Extraterrestrial 2. Deep oceans 3. Antarctic region 4. Subterranean CO_2 Captured by Acid./Degas. 1. Extraterrestrial 2. Deep oceans 3. Antarctic region 4. Subterranean
III. MAJOR INDUSTRIAL CO_2 EMISSION SOURCES (e.g. fossil plant stacks)	CO_2 Captured by Liquids - same alternatives as for atmosphere CO_2 Captured by Solids - same alternatives as for atmosphere CO_2 Captured by Refrigeration - same alternatives as for atmosphere CO_2 Removed by Adv. Power Cycle 1. Extraterrestrial 2. Deep oceans 3. Antarctic region 4. Subterranean

Table 5C

OPTIONS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE
OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT	OPTIONS FOR RECOVERING CAPTURED CO_2
I. ATMOSPHERE	$\underline{CO_2\ Captured\ by\ Liquids}$ 1. Desorption by flashing 2. Desorption by distillation 3. Strip with gases, i.e., H_2, N_2, steam, etc. 4. Desorption by combined flashing and distillation or stripping 5. Electrolytic decomposition of sodium carbonate to form sodium hydroxide, H_2, O_2, and CO_2 by non-fossil fuel source $\underline{CO_2\ Captured\ by\ Solids}$ 1. Decomposition by heating a/o stripping (e.g. by high pressure steam) $\underline{CO_2\ Captured\ by\ Methanation}$ 1. Absorb methane in a solvent, then desorb by flashing a/o distillation or stripping
II. OCEANS	
III. MAJOR INDUSTRIAL CO_2 EMISSION SOURCES (e.g. fossil plant stacks)	$\underline{CO_2\ Captured\ by\ Liquids}$ – same alternatives as for the atmosphere. $\underline{CO_2\ Captured\ by\ Solids}$ – same alternatives as for the atmosphere. $\underline{CO_2\ Captured\ by\ Refrigeration}$

Table 5D

OPTIONS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE

OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT	OPTIONS FOR DISPOSAL OF RECOVERED CO_2

I. ATMOSPHERE

Gaseous CO_2
1. Extraterrestrial

Liquid CO_2
1. Extraterrestrial
2. Deep oceans
3. Subterranean

Solid CO_2
1. Extraterrestrial
2. Deep oceans
3. Antarctic region
4. Subterranean

II. OCEANS

III. MAJOR INDUSTRIAL
     CO_2 EMISSION
     SOURCES (e.g.
     fossil plant
     stacks)

OPTIONS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE
OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT	REUSE ALTERNATIVES FOR CAPTURED/RECOVERED CO_2

I.   ATMOSPHERE

Gaseous CO_2
1. Catalytically convert CO_2 to gaseous a/o liquid carbonaceous fuels (methane, methanol, gasoline) by reaction with hydrogen, using non-fossil energy source (e.g. fission, fusion, solar)
2. Decomposition of CO_2 to CO using non-fossil energy source (e.g. solar and nuclear radiation and high temperature heat), shift CO with water to form CO_2 and H_2; subsequently convert to carbonaceous fuels
3. React CO_2 with NH_3 to form urea fertilizer
4. Use CO_2 for controlled photosynthesis in greenhouses--plant products in biosphere a/o burn for energy production

Liquid CO_2
1. Use for liquid CO_2 applications including industrial chemical uses
2. Use for displacing crude oil from reservoir rock.
3. Same alternatives as for gaseous CO_2 after vaporization

Solid CO_2
1. Use for dry ice applications
2. Same alternatives as for gaseous CO_2 after sublimitation

II. OCEANS

III. MAJOR INDUSTRIAL CO_2 EMISSION SOURCES (e.g. fossil plant stacks)

Fuel Type	Chemical Formula	Higher Heating Value BTU/lb	CO_2 generated lb CO_2/lb fuel	CO_2 generated lb CO_2/1000 BTU	Energy generated kwh(e)/lb CO_2 generated
Coke (ashless C)	C	14,100	3.67	0.26	
Bituminous Coal	$CH_{0.8}O_{0.1}$	13,000	2.75	0.21	0.56
Gasoline & Fuel Oil (petrol. dist.)	$(CH_2)_n$	20,800	3.14	0.15	0.90
Benzene	C_6H_6	18,000	3.38	0.19	
Acetylene	C_2H_2	21,500	3.38	0.16	
Methanol (wood alc)	CH_3OH	10,000	1.38	0.14	
Methanol (syn. from coal)	CH_3OH	10,000	2.75	0.28	0.42
Biomass (wood, cellulose)	$(CH_2O)_n$	8,000	1.47	0.18	
Carbon Monoxide	CO	4,370	1.57	0.36	0.33
Natural Gas	CH_4	24,100	2.75	0.11	1.07
SNG from coal gasification	CH_4	24,100	8.75	0.34	1.01
SNG Coal & Nuclear Hydrogen	CH_4	24,100	2.75	0.11	1.07
Hydrogen generated by:	H_2	61,000	0	0	
Coal Gasification	H_2	61,000	16.5	0.27	
Natural Gas Reforming	H_2	61,000	7.0	0.11	
Nuclear-Electrolytic	H_2	61,000	0	0	
Solar-Electrolytic	H_2	61,000	0	0	
Geothermal-Electrolytic	H_2	61,000	2.44	0.04	

Finally it is noted that synthetic natural gas (SNG made from coal) and carbon monoxide (CO) generates the largest amount of CO_2 per unit of energy released. Hydrogen produced by coal gasification generates less CO_2 than SNG from coal. In determining the CO_2 generated by synthetic fuels such as SNG, methanol and hydrogen from coal, the CO_2 generated in the production process is included. Thus, CO_2 generated from SNG (0.34) is 3 times greater than CO_2 generated from natural gas (0.11). Geothermal energy releases certain amounts of CO_2 per unit 1000 BTU which is estimated from a number of operating geothermal wells.[10] Of course there is no CO_2 generation if nuclear or solar energy is used to produce hydrogen fuel.

Control Source CO_2 Concentrations

Table 7 lists the CO_2 concentration ranges of CO_2 sources and control points including, the atmosphere, the ocean, and the industrial emitters including natural wells used for energy sources. The concentration of CO_2 in the atmosphere and in the oceans are fairly constant around the globe. The concentration by weight in the atmosphere is about 5 times that in the ocean, however, because the ocean is about 1000 times denser than the atmosphere the total mass in a given volume in the ocean is about 200 times greater. The concentration of CO_2 in industrial emissions are about 10^3 to 10^4 times greater than that in the atmosphere. Thus, the energy required to

different sources is indicated in Table 7. The minimum energy is inversely
proportional to the logarithm of the volumetric source concentration, so
that theoretically it should take 3 to 5 times more energy to extract CO_2
from the atmosphere than from stacks of fossil fueled plants. Because of
other inefficiencies and frictional losses, the relative energy requirements
increases much more than the logarithmic proportionality as the concentration
of the source decreases.

Table 7

CO_2 CONCENTRATIONS AT CONTROL POINTS AND MINIMUM
CO_2 SEPARATION ENERGIES

Control Point	CO_2 Concentration		Min. Separation Energy[*]
	% by Vol.	% by Wt.	kwh/lb CO_2
Atmosphere	331×10^{-4}	502×10^{-4}	0.0570
Ocean	66×10^{-4}	100×10^{-4}	0.0570
Industrial Emitters			
Fossil Fueled Power Plants	7-20	11-28	0.0259-0.0179
Chemical Plants (lime, cement, NH_3, coal gasif.)	20-100	28-100	0.0179-0.000
Metallurgical Plants (blast furnaces)	20	28	0.0179
Natural Gas Wells	0-50	0-73	0.0099
Geothermal Wells	~50	~66	0.0099

[*]Minimum Energy based on free energy of mixing:

$$\Delta F = RT\Sigma n_i \ln \frac{P_i}{P_i^o}$$, where P_i^o and P_i are the initial and final partial pressures

of the i^{th} species, respectively. R is the gas constant, T is temperature in

degrees absolute and n_i is the number of moles of the i^{th} species.

CO_2 Removal and Recovery Processes

a) The atmospheric and oceanic control points

Taking the atmosphere as the CO_2 control point one can estimate the
amount of energy needed to remove and recover CO_2. This has been done in a
previous study[6] for a number of options. Results are summarized in Table 8.

pressurized systems.

<div align="center">

Table 8

ENERGY REQUIRED TO REMOVE AND RECOVER CO_2

FROM THE ATMOSPHERE AND SEA WATER[6]

</div>

CO_2 Removal and Recovery Process	Energy for CO_2 Separation kwh(e)/lb CO_2
1. H_2O absorption/stripping (atm. pressure)	1.0
2. H_2O absorption/stripping (20 atm)	9.7
3. Methanol adsorption/stripping (20 atm and $-80^\circ F$)	7.3
4. Aqueous K_2CO_3 absorption/stripping (atm pressure)	0.4
5. CO_2 adsorption/desorption	6.1
6. Cryogenic Separation	9.2
7. Caustic absorption/electrolytic stripping (isothermal process)	0.9
8. Stripping of sea water	0.4

Note: For a bituminous coal burning power plant supplying power for
for removal of CO_2 in system 4 (aq. K_2CO_3), CO_2 generated/CO_2
removed = 0.4/0.56 = 0.71 and net CO_2 reduction/CO_2 removed =
1-0.71 = 0.29. At 100% CO_2 removal efficiency, net power
plant efficiency would be reduced from 38% to 10%.

The most energy economic system is the dilute aqueous alkaline K_2CO_3
system at atmospheric pressure because it has considerably higher solubility
for CO_2 than water. An advanced isothermal system is also estimated using
electrolytic decomposition of a carbonate-bicarbonate solution to release CO_2
and regenerate the alkaline carbonate solution to scrub the atmospheric CO_2.
The seawater stripping system has a low energy requirement because seawater

non-fossil fuel power plant. By comparing the CO_2 generated per unit energy produced for a fossil fueled plant from Table 6, with the energy required to recover the CO_2 shown in Table 8 one can estimate the ratio of CO_2 produced to CO_2 recovered. Thus, for all the processes listed in Table 8, with the exception of the aqueous K_2CO_3 scrubbing and seawater stripping, more CO_2 would be generated than recovered if a coal burning power plant were used to supply the electrical power. However, even in the K_2CO_3 scrubbing case there is a significant penalty in energy generation efficiency. The conclusion to be reached here is that only a non-fossil fueled power plant such as nuclear or solar is allowable to generate the necessary electrical power for removal of CO_2, from the atmospheric and ocean control points.

b) The industrial control points

For the more concentrated industrial emission streams, less energy is required to recover the CO_2. Therefore, there is a larger margin for net CO_2 recovery if fossil fuel is used to power the CO_2 separation processes. However, estimates of energy requirements shown in Table 9 indicate that only for the high capacity solvent absorption/stripping processes (i.e. K_2CO_3, MEA, caustic scrub) are the energy requirements low enough to allow fossil fuel power plants to supply power for the separation process. However, even use of these high capacity solvents will tend to reduce power plant efficiency as indicated in note (3) of Table 9.

Disposal of CO_2

The removal and recovery of CO_2 is only the first step in the environmental control chain. Disposal is probably the most critical step. Tables 5A through 5E lists a number of disposal schemes. The disposal breaks down into several ultimate possibilities.

1. Burial in the deep ocean

In the two-box model, the world ocean is represented by two reservoirs, separated by a thermocline. One reservoir consists of surface layers to a depth of about 100 meters; the other, of deeper layers from the 100 meter depth to the ocean floor. Mixing is assumed to occur rapidly within each box or reservoir, but exchange between the two boxes proceeds slowly. Thus, the deep ocean represents a sink for CO_2 since there is no direct exchange between the atmosphere and the deep ocean. The main discrepancy between the simple two-box model and the real ocean is that in some regions (e.g. Artic, Antartic and Gibraltar regions) convection currents extend from the ocean surface to the ocean bottom.

One proposal for disposing of collected CO_2 is to inject it into the sea at the Strait of Gibraltar.[4] Presumably, the current would carry it to the deeper ocean waters where it would remain for centuries. Another proposal is to inject liquid CO_2 into the deep sea at a density greater than that of deep sea water via a long pipe. The CO_2 would sink to the bottom of the ocean forming a liquid CO_2 lake within the ocean.

CO_2 Removal and Recovery Process	Energy for CO_2 Separations kwh(e)/lb CO_2 [2]
1. Aqueous K_2CO_3 absorption/stripping	0.1 [3]
2. Caustic absorption/electrolytic stripping (isothermal process)	0.2
3. Amine absorption/stripping	0.1
4. Adsorption/desorption on molecular sieves	0.6
5. Cryogenic Separation	1.8
6. Absorption in sea water [1]	0.6 [1]

Note:

(1) @60% CO_2 removal efficiency and including deep ocean disposal of captured CO_2

(2) For coal burning plant energy output per unit CO_2 generated is 0.56 kwh(e)/lb CO_2; any removal system requiring values equal to or greater than this yields no reduction in net CO_2 emitted.

(3) For a K_2CO_3 removal system (process 1), the overall power plant efficiency would be affected as follows:

CO_2 Removal Efficiency - %	Net Power Plant Efficiency - %	Lb CO_2 Discharged To Atmosphere Per Net kwh(e) Generated
100	31.0	0
85	32.0	0.33
75	33.5	0.52
60	33.8	0.82
50	34.5	1.01
25	36.3	1.44
0	38.0	1.83

The current release rate of fossil carbon to the atmosphere is about 5×10^{15} g/yr, whereas the current carbon content of the deep ocean is estimated at 0.373×10^{20} g. Therefore, if all of this fossil carbon was collected and deposited in the deep ocean, the quantity of carbon contained therein would increase by about 0.013% per year.

options. The reinjection into the atmosphere due to escape from the mines or by equilibrating a high CO_2 concentration on natural zeolite, is of main concern with this method of disposal.

3. Extraterrestrial burial

CO_2 packaged as solid, liquid or high pressure gas would be sent by rocket beyond the escape velocity of the earth or possibly to other planets. In this way one can assure that the CO_2 would not gravitate back to earth. If non-fossil generated hydrogen is used as rocket fuel no exhaust CO_2 penalty would be incurred, however, energy costs would be excessive.

4. Recycle in products

Although a number of CO_2 containing commercial products can be made for the economy, i.e. dry ice, soda ash, inorganic carbonates, urea, the CO_2 remains about the same because fossil energy is used to produce them and the markets for the products are limited.

A unique disposal method is to convert the recovered CO_2 to synthetic liquid and gaseous carbonaceous fuel using a non-fossil energy source, for example, nuclear power. In this way, the CO_2 can be reused thus reducing the CO_2 buildup in the atmosphere. There are several options in applying this carbon-nuclear cycle.[8,9]

(a) Coal can be converted to SNG, oil, and gasoline using nuclear power based electrolytic hydrogen. The nuclear hydrogen would be used directly to hydrogenate the coal. In this manner the CO_2 buildup would be reduced by a factor of 3 compared to the natural gas and petroleum cases.

(b) Remove and recover CO_2 from coal burning power plants and combine with nuclear electrolytic hydrogen to produce methanol which can be dehydrated to gasoline on zeolite catalysts.[11] Figure 3 shows a flowsheet of the system. In this manner, power is produced from the fossil plant and the carbon in the CO_2 reused in producing synthetic carbonaceous fuel.

(c) Remove and recover CO_2 from the atmosphere and combine with electro-lytically produced hydrogen to form synthetic carbonaceous fuels. A flow-sheet of the system is shown in Figure 4 and features a novel isothermal (electrolytic) system for regenerating the CO_2 and caustic scrub soluticn in addition to the product hydrogen.

A quantitative estimate of the number of nuclear reactors needed to convert the CO_2 emissions from industrial stack emissions to synthetic carbonaceous fuels for the transportation sector in the US is shown in Table 10.[8] The data indicates that there is more than enough CO_2 emitted from fossil energy power plants to supply the needs of the automotive industry and that about one thousand 1000 MW(e) nuclear reactors would be needed to make the total conversion.

REACTIONS:

POTASSIUM CARBONATE CO_2 RECOVERY PROCESS
$CO_2 + K_2 CO_3 + H_2O \rightleftharpoons 2 KHCO_3$

ELECTROLYSIS
$3 H_2O = 3 H_2 + \frac{3}{2} O_2$

CATALYTIC CONVERTOR
$3 H_2 + CO_2 = CH_3OH + H_2O$

CATALYTIC DEHYDRATION
$n CH_3OH = (CH_2)_n + n H_2O$
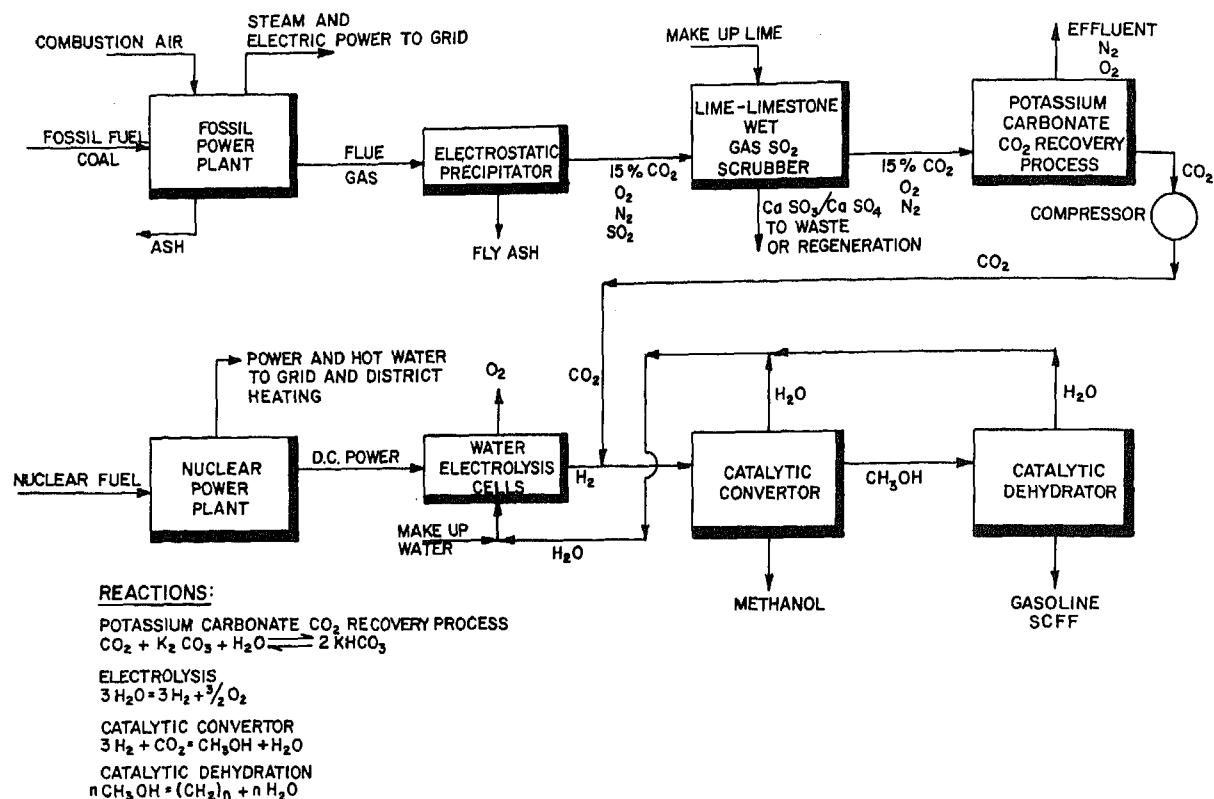
A potential large scale use for CO_2 is in tertiary treatment of depleted oil wells, however, this application may be of limited value as a long term disposal method. Another recycle system is to utilize the CO_2 as a diluent with oxygen in a fossil fuel power plant so that the only effluent is CO_2 thus reducing energy requirements for removal and recovery. With this system a compact highly efficient power plant can be designed. The plant can be sited in highly populated areas and the CO_2 removed for disposal in remote areas.

Finally, an all nuclear or solar-electric hydrogen economy would essentially reduce CO_2 emissions to a negligible level.

NaOH → AIR 'OUT'

CAUSTIC AIR SCRUBBER

AIR 'IN' (CO₂ IN ATM.)

Na₂CO₃

O₂ 'OUT'

CO₂   CO₂ + H₂

NUCLEAR POWER REACTOR

ELECTRICAL TURBO GENERATOR

D.C.

ELECTROLYTIC CARBONATE CELLS   H₂

CATALYTIC CONVERTOR

NaOH

H₂O

CH₃OH

U FUEL

MAKEUP H₂O

H₂O

CATALYTIC DEHYDRATOR

H₂O

(CH₂)ₙ

GASOLINE SCFF

$$2NaOH + CO_2 \xrightarrow[\text{ABSORPTION}]{\text{ATMOSPHERIC}} Na_2CO_3 + H_2O$$

$$Na_2CO_3 + 4H_2O \xrightarrow[\text{ELECTROLYSIS}]{} 2NaOH + 3H_2 + \tfrac{3}{2}O_2 + CO_2$$

$$3H_2 + CO_2 \xrightarrow[\text{REACTION}]{\text{CATALYTIC}} CH_3OH + H_2O$$

$$n\, CH_3OH \xrightarrow[\text{DEHYDRATION}]{\text{CATALYTIC}} (CH_2)_n + n\, H_2O$$
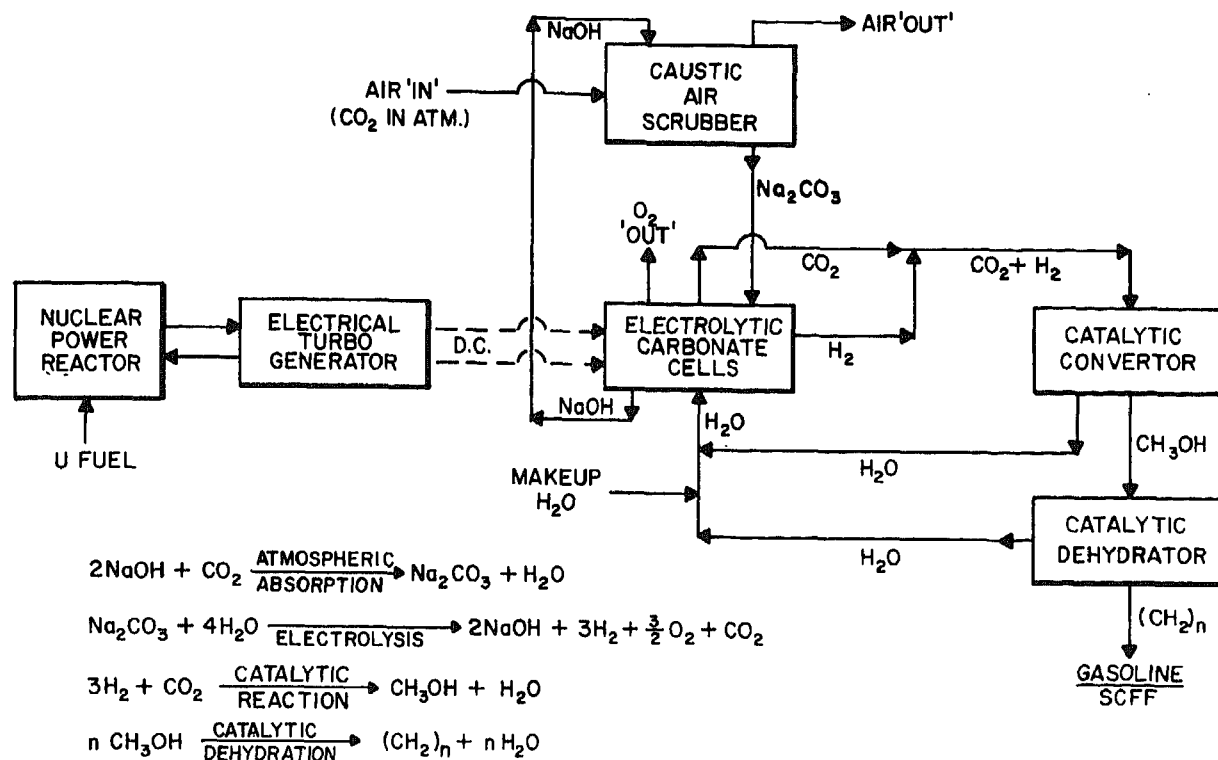
Table 10

INDUSTRY RESOURCE CAPACITY TO PRODUCE SYNTHETIC CARBONACEOUS FUELS
AND FEEDSTOCKS FROM EFFLUENT CO AND CO₂ FEEDSTREAMS AND NUCLEAR POWER[9]

Based on 1975 Production Capacities

Industry	Production capacity Millions tons/yr	CO_2 or CO availability Millions tons/yr	Gasoline production capability Billions gal/yr	No. of 1000 MW(e) nuclear power plants required
Lime and Cement	25 Lime 85 Cement	86 CO₂	9	90
Steel	125 Steel	125 CO	20	125
Coal for Power	500 Coal	1,560 CO₂	165	1,680
Gasoline, US Consumption		(945 CO₂)[1]	100	(1,000)[1]

1) Capacity needed to meet 1975 US consumption of gasoline of approximately 100 billion gal/yr.

growing global technological population, the following environmental control measures can be recommended.

(1) Attempt to find and utilize more natural gas (and petroleum) in preference to coal because of its 2 to 3 times lower CO_2 emissions per unit energy produced.

(2) Consider recovering the more concentrated CO_2 industrial stack gas emissions using fossil fuel power.

(3) Attempt recovering the less concentrated atmospheric and oceanic CO_2 using nuclear power or another non-fossil power source such as solar.

(4) Consider disposal of the CO_2 by deep ocean burial.

(5) Combine coal with nuclear electrolytic hydrogen to produce SNG.

(6) Produce synthetic carbonaceous fuel from atmospheric CO_2 and nuclear electrolytic hydrogen.

(7) Convert to a hydrogen economy using a non-fossil energy source.

(8) Convert to an all electrical economy substituting nuclear or another non-fossil fuel source such as solar.

(9) Convert to a biomass - photosynthetic energy economy.

Since no energy source is truly benign, in the long run, the realistic ECT scenario for CO_2 will depend on the lesser of the evils in selecting and utilizing our energy source alternatives.

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1. INTRODUCTION

If we burn fossil fuels at too rapid a rate in the future, there is a real threat of unacceptable consequences from increasing levels of atmospheric carbon dioxide. While the uncertainties involved are large, there are ample reasons for concern:

Atmospheric carbon dioxide is increasing.

The rate of fossil fuel consumption has increased exponentially for 120 years.

The reserves of fossil carbon are very large.

The oceans can take up carbon dioxide from the atmosphere at only a limited rate.

The magnitude of the greenhouse effect may be several degrees Celsius per doubling of atmospheric carbon dioxide.

If we do not limit the rate of fossil fuel consumption in the future, it seems essential to consider, as Dr. Steinberg has outlined in his paper, possible means of controlling the excess carbon dioxide produced.

The goal of our study, which is still underway, has been to examine in more detail the technical feasibility, monetary cost and energy cost of some of the more promising means of capture and disposal. Specifically we have restricted ourselves to the collection of carbon dioxide from stationary sources such as power plants, though these amount to only 20 to 30% of the total fossil carbon dioxide flux, and the only means of disposal we have considered in any detail is ocean disposal.

The energy costs and dollar costs of collecting carbon dioxide from stack gas by present technology have been estimated by Pappano et al. (1976) and by Rump et al. (1977) for large scale operations (in the later case, 270 metric tons of CO_2/hr) for enhanced oil recovery. In Table I, these energy costs are compared with the energy worth of the carbon dioxide, i.e., the energy derived by burning the coal that produced it. We have assumed a coal (Sewanee Coal from Grundy Co., Tenn.), one metric ton of which produces 6.79 million kcal of heat and 2.55 metric tons of carbon dioxide. This gives a cost of CO_2 recovery that is about 46% of the energy worth. The dollar cost is estimated at about $19 per metric ton of CO_2 ($1.80/million BTU).

The estimated energy cost of compression to 150 atm and transporting 25 miles are small by comparison. The estimated energy costs of conversion into solid forms such as dry ice or the hydrate are more appreciable, 14 to 18% of the energy worth of the carbon dioxide. The dollar costs of these steps are proportionately higher because much of the energy consumed is electrical.

TABLE I. COST OF COLLECTING AND PROCESSING CO_2 FROM STACK GAS

	$\dfrac{10^6 \text{ kcal}}{\text{Metric Ton of } CO_2}$	% of CO_2 [b] Energy Worth	\$/Metric Ton of CO_2
Capture of CO_2 [a]	1.23	46	19
Compress to 150 atm, [a] Transport 40 km	0.10	4	4
Solidify CO_2 [c]			
To Dry Ice	0.36	14	14
To $CO_2 \cdot 6H_2O$	0.47	18	17

[a]Rump et al. (1977). 290 metric tons CO_2/hr, MEA process.

[b]One metric ton of coal assumed to yield $6.79 \cdot 10^6$ kcal and 2.55 metric tons of CO_2.

[c]Calculated from data of Stickney (1932).

3. COMBUSTION IN OXYGEN

Marchetti (1978) has suggested that coal be burned in pure oxygen to produce nearly pure carbon dioxide and water, thus avoiding the costly collection from flue gas. Table II summarizes the comparable costs of this alternative.

	Metric Ton of CO_2	Energy worth
Preparation of Pure Oxygen[a] (22 atm)	0.76	29
Increase in Plant Efficiency (38% to 42%)	-0.28	-11
Net Cost	0.48	18
Capture CO_2 From Stack Gas	1.23	46

[a]From data supplied by P. Koster, Linde Div., Union Carbide Corp.

The major cost is, of course, the separation and compression of oxygen from air, amounting to 400 kWh of mostly electrical energy per metric ton of oxygen. Since 2.15 metric tons of oxygen are required to burn one metric ton of our coal, this amounts to 1.95 million kcal/metric ton of coal (assuming 38% efficiency for the production of the electricity). Thus the oxygen production costs amount to 0.76 million kcal/metric ton of CO_2, considerably less than the cost of recovering CO_2 from normal flue gas.

Moreover, it is reasonable to expect there will be an increase in plant efficiency from (1) the reduction in heat loss to the stack gas, (2) the elimination of the combustion air fans, (3) perhaps an increase in combustion temperature. If an improvement in overall efficiency from 38% to 42% were possible, this would amount to 0.28 million kcal/metric ton of $CO_{\underline{\ }}$ which could be credited against the production costs of the oxygen.

An additional possible advantage of combustion in pure oxygen is that there may be no need for an SO_2 scrubbing step which otherwise would precede the CO_2 scrubber. The CO_2 and SO_2 could be compressed and disposed of together.

4. OCEAN DISPOSAL

If carbon dioxide can be delivered to the deep oceans this would give a retention time of the order of a thousand years even if this acidic gas did not react with the basic minerals present such as calcium carbonate. We will consider various forms of carbon dioxide that would be denser than seawater and have a vapor pressure lower than the hydrostatic pressure at the depth of injection.

it does not change much with temperature, remaining in the range 1.3 to 1.5 moles/kg. As can be seen in the table, dissolving carbon dioxide in water increases the density. The apparent molar volume of dissolved CO_2 (measured before the turn of this century and cited by Eley, 1939) is about 35 cm^3. The density increase at the maximum solubility is only about 1%, however, not enough to exceed the density of seawater. Hence fresh water does not seem suitable as a medium for the disposal of carbon dioxide in the ocean.

TABLE III. THE CO_2 CONTENT AND DENSITY OF WATER AT
THE LIQUEFACTION PRESSURE OF CO_2

Temp. (°C)	Vapor Pres. of Liq. CO_2[a] (atm)	Dissolved CO_2[b] (Moles/kg H_2O)	Conc.[b] (Wt %)	$\frac{\rho(Sol'n)}{\rho(H_2O)}$[c]
0	34.4	1.45	6.02	1.0125
5	39.1	1.36	5.64	1.0117
10	44.4	1.29	5.37	1.0111
15	50.2	1.25	5.22	1.0108
20	56.5	1.24	5.16	1.0106
25	63.5	1.25	5.22	1.0108
30	71.2	1.29	5.39	1.0111

[a] Vukalovich and Altunin (1968), p. 97.

[b] Based on data in Linke (1958), p. 460.

[c] Calculated assuming the molar volume of dissolved CO_2 is 35 cm^3.

4.2 Carbon Dioxide in Seawater

The solubility of carbon dioxide in seawater as a function of pressure up to the liquefaction pressure at various temperatures is shown in Fig. 1. Assuming conservatively that the molar volume is no larger in seawater than it is in fresh water, there should be a substantial density increase, for example, 0.0075 g/cm^3 at a concentration of 1 mole/kg. The minimum depth of injection without the formation of bubbles is shown on the upper scale.

To consider further the disposal of carbon dioxide in seawater, let us imagine the simple system shown in Fig. 2: Water is taken in at a temperature of t_1 and density ρ_1 which depend on the location and depth chosen; it is pumped through a gas-liquid contactor where CO_2 is dissolved to a concentration C, the density rises to ρ_3 and because of the heat of solution the temperature
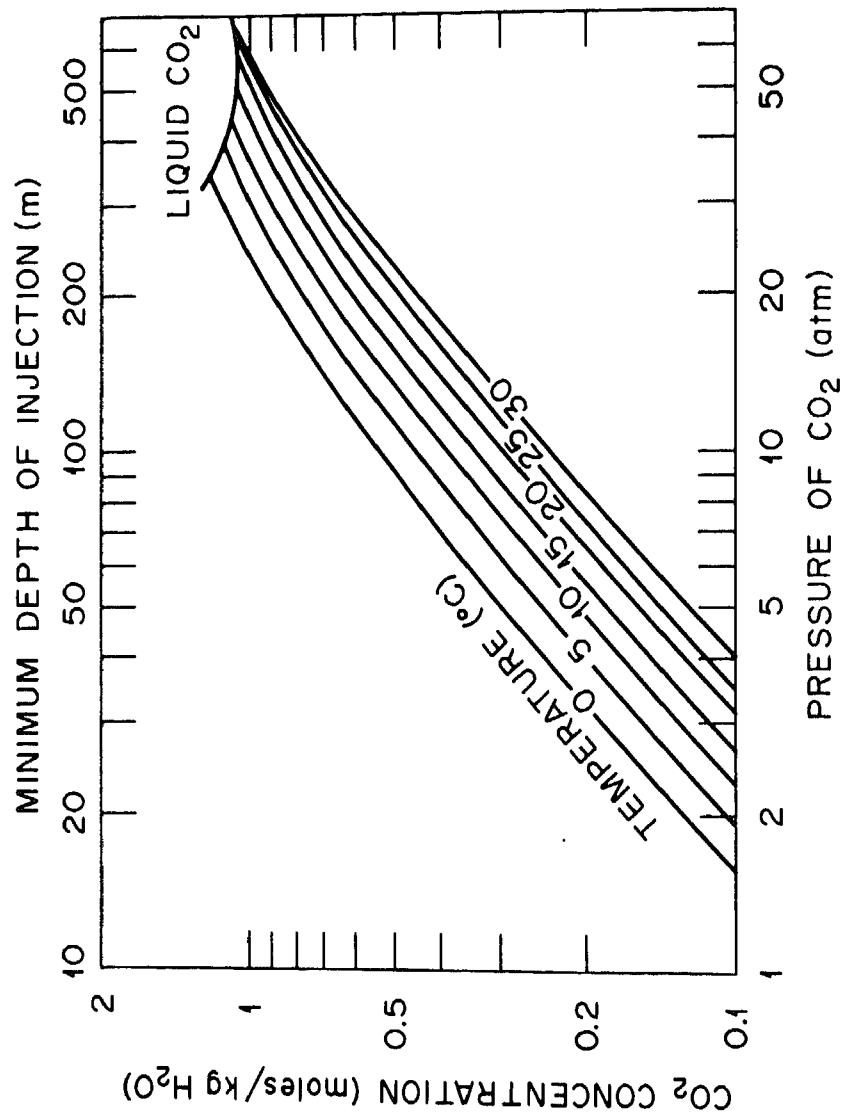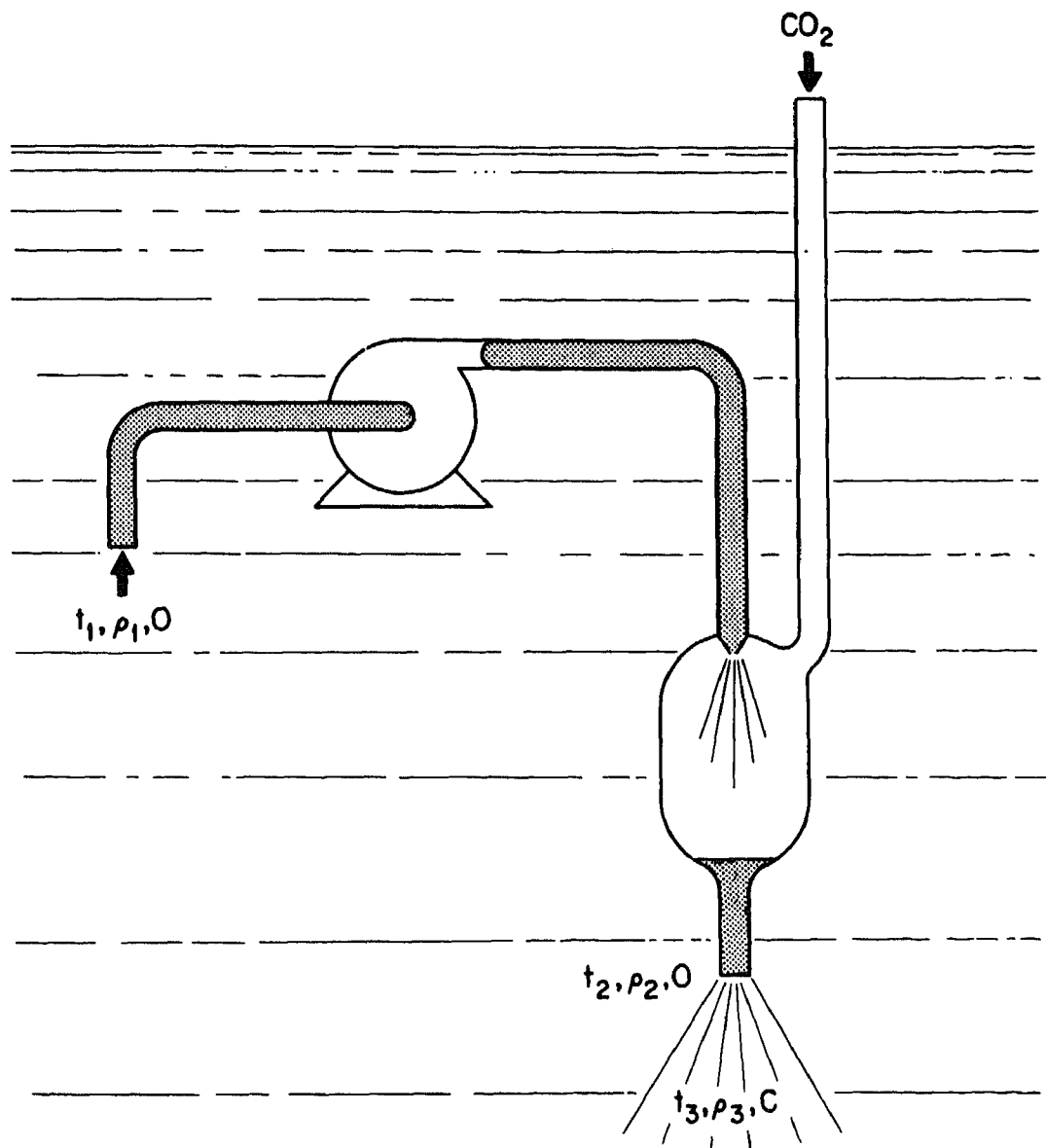
Fig. 1. Solubility of CO₂ in Seawater

Fig. 2. Schematic Representation of the Injection of CO_2 into Seawater

The temperature t_3 can be estimated from the relationship

$$t_3 = t_1 + 5 \cdot C , \tag{1}$$

based on a heat of solution of 5 kcal/mole. The density difference at the outlet, $\rho_3 - \rho_2$, can be calculated as the sum of two terms.

$$\rho_3 - \rho_2 = [\rho(t_3, 0) - \rho(t_2, 0)] + [\rho(t_3, C) - \rho(t_3, 0)] . \tag{2}$$

The first is the density decrease caused by heating the ambient seawater from t_2 to t_3, known accurately from data for seawater. The second term is the density increase produced by introducing the carbon dioxide to a concentration of C moles/kg, and can be estimated from the approximation

$$\rho(t_3, C) - \rho(t_3, 0) \cong 0.0072 \cdot C , \tag{3}$$

based on a molar volume of 35 cm^3.

It turns out that the density difference, $\rho_3 - \rho_2$, which we wish to maximize depends on two quantities, the inlet temperature t_1 (which should be minimized) and the concentration of carbon dioxide C (which should be maximized). The calculations plotted in Fig. 3 were done assuming the injection point was at the bottom of the thermocline ($\sim$ 1,000 m depth) where the water temperature becomes approximately constant below 5°C. Injection at lesser depth would give larger density differences because the ambient water temperature is higher.

One of our early ideas for the disposal of carbon dioxide from a coal-fired power plant was to take advantage of the cooling-seawater requirements of an ocean thermal energy conversion (OTEC) plant. A 1,000 MW(e) coal-fired plant produces about 210 kg/sec of carbon dioxide. If this were dissolved in seawater to a concentration of 0.5 moles/kg, about 10,000 kg/sec of water flow would be required. A 100 MW(e) OTEC plant proposed by TRW Inc. would require 380,000 kg/sec of cooling water. This is 38 times the flow rate required to dissolve the CO_2 released by a 1,000 MW(e) fossil fuel plant, and we thus conclude that there would be no advantage in using the OTEC plant. The same benefit could be gained by siting the fossil plant on a floating platform or at a coastal location where the CO_2-seawater solution could be discharged at the proper depth. Indeed the seawater requirements for such disposal are so modest that if deep ocean water were used for cooling the condenser of a coal-fired plant, it could carry away all the carbon dioxide produced by the plant at a concentration of the order of 0.1 moles/kg while at the same time offering greater thermal efficiency because of its lower temperature.

4.3 Carbon Dioxide Hydrate

The hydrate of carbon dioxide has a clathrate structure (Miller and Smythe, 1970) with a density of about 1.12 g/cm^3, greater than that of seawater. If large blocks of the solid were dropped into the sea they would sink rapidly.
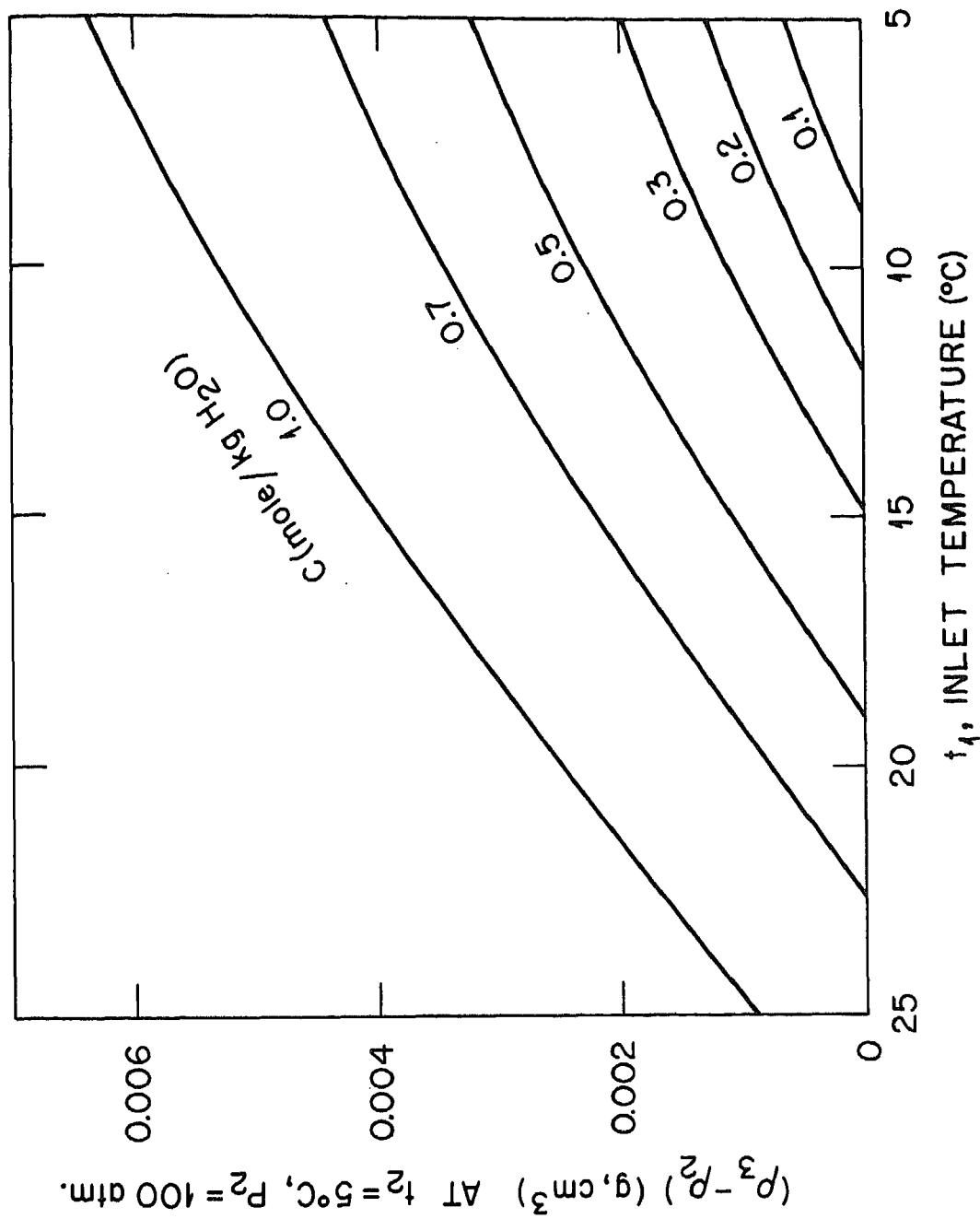
Fig. 3. The Excess Density of a CO_2 Disposal Stream in Seawater

static pressure is about 50 atm and the temperature _____, g_____ ____
formation would cease. The reaction product thereafter would be a carbon
dioxide-seawater solution more dense than the surrounding water. The reaction
rate might be slow enough to permit the block to reach the bottom before an
appreciable fraction had been consumed.

4.4 Liquid Carbon Dioxide

Marchetti (1976) has mentioned a suggestion of Nordhaus for disposal in the
form of liquid carbon dioxide. In Fig. 5 we see that while the density of the
liquid is less than that of seawater at the surface, it is much more compressible
and has a much higher thermal coefficient of density. From these curves it
appears, however, that a considerable depth of injection would be necessary,
about 3,000 meters, to insure that the CO_2 is more dense than the surrounding
seawater.

4.5 Dry Ice

This form has the greatest density, about 1.5 g/cm^3, and would be the most
economical to transport by water. Large blocks of it would sink rapidly and,
again, once past a depth of about 500 m, bubbling should cease and the reaction
products - the hydrate, the liquid and dissolved CO_2 - should be denser than the
surrounding water. This form of carbon dioxide might survive the trip to the
ocean bottom best of all.

5. SUMMARY AND CONCLUSION

1. The cost of CO_2 recovery from flue gas will be high.

2. Combustion of fuel in pure oxygen may permit a more efficient recovery of
   CO_2 (and SO_2).

3. Deep ocean disposal would give a long retention time.

4. Fresh water is not a suitable medium for ocean disposal.

5. Seawater could be used because dissolving CO_2 should increase the density
   of seawater.

6. The cooling water flow from one OTEC plant could accommodate the CO_2 output
   of hundreds of fossil fuel plants of the same capacity.

7. The cooling water flow from a fossil fuel plant is more than adequate to
   accommodate the CO_2 output of the plant, but the plant must be sited to per-
   mit ocean disposal.

8. We need more data on the density effect of introducing CO_2 into seawater as
   a function of temperature and pressure.
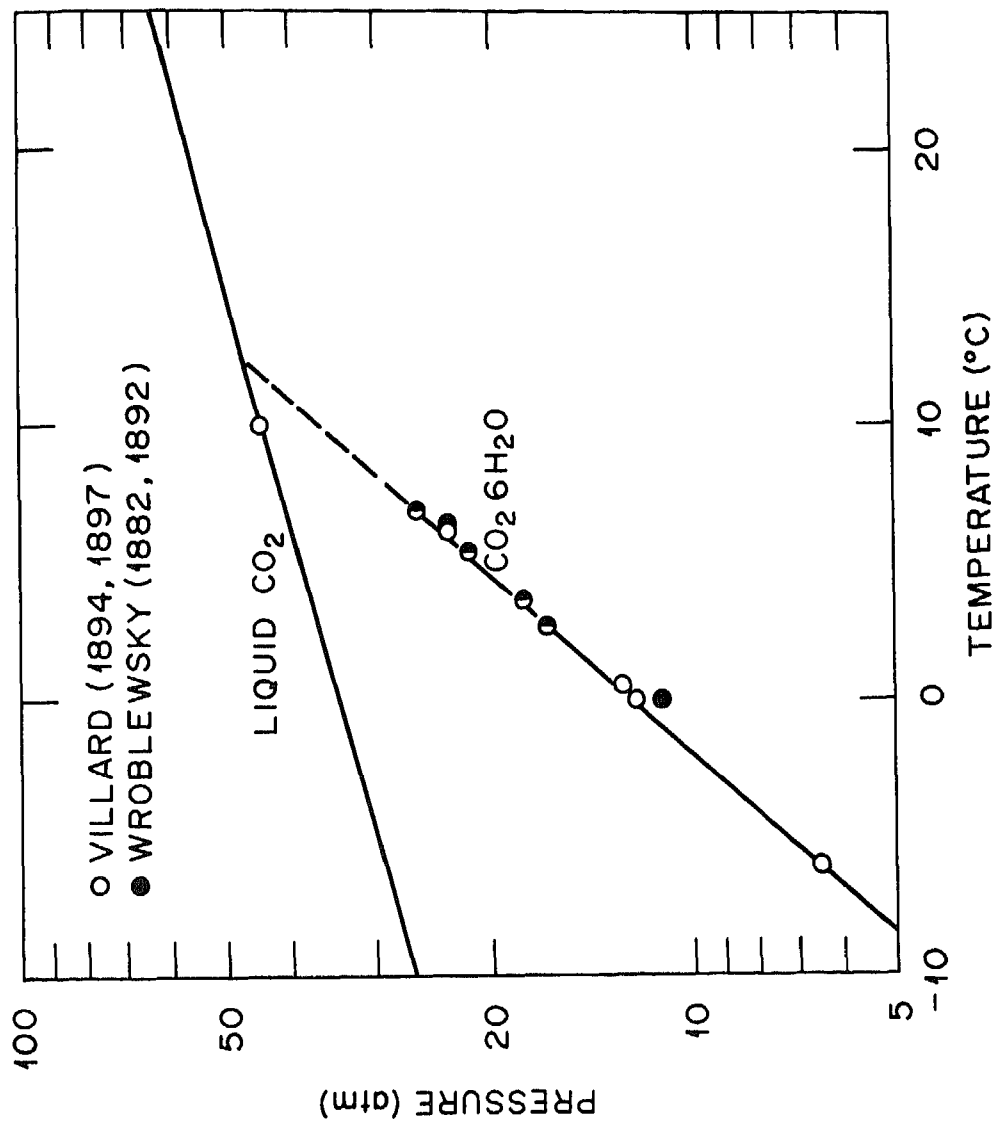
Fig. 4. Vapor Pressure of Liquid CO_2 and CO_2 hydrate. Data Cited by Quinn and Jones (1
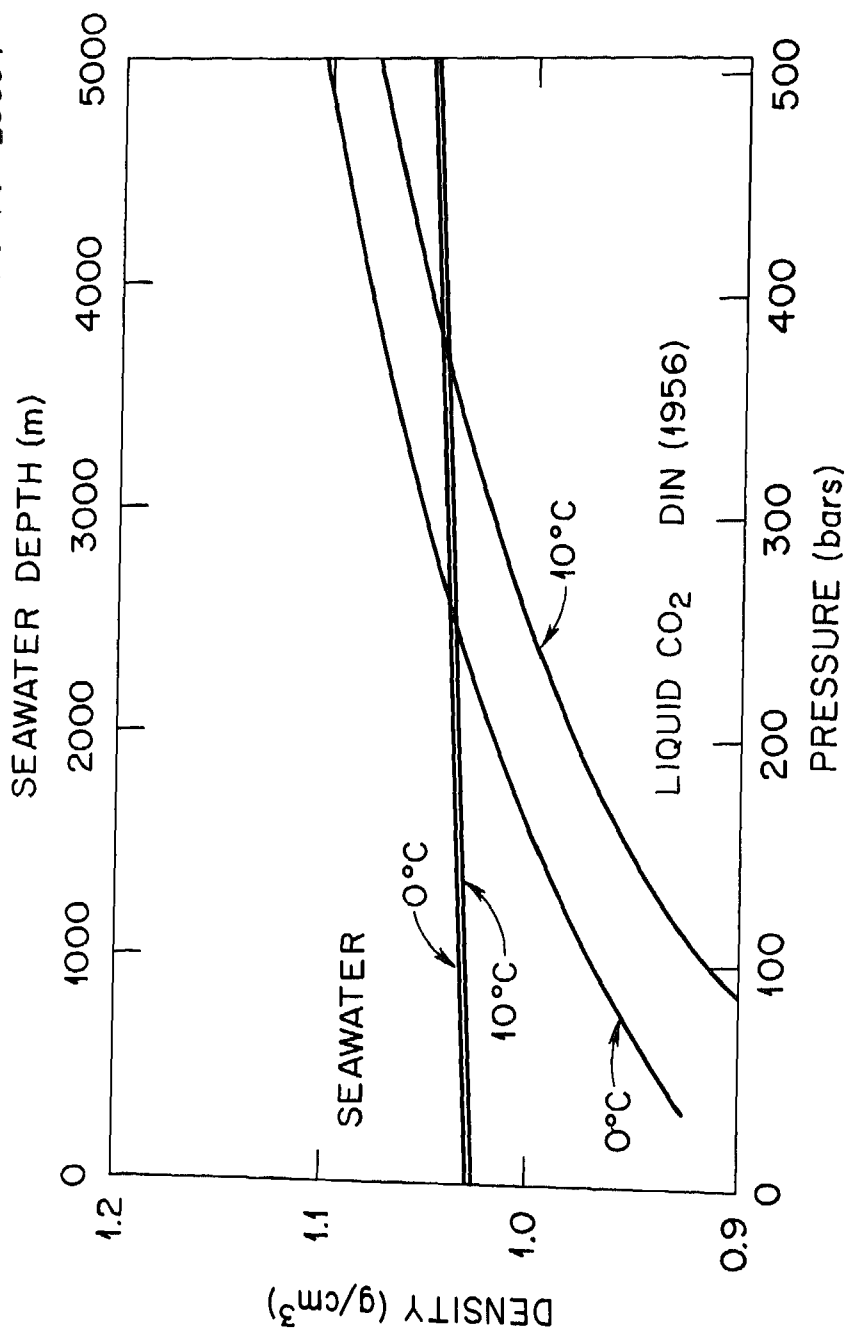
Fig. 5. A Comparison of the Densities of Liquid CO_2 and Seawater

10. Other forms of CO_2 suitable for disposal may include the hydrate and dry ice.

11. Liquid CO_2 might be used for ocean disposal, but the depth of injection would be over 3,000 m.

ACKNOWLEDGMENT

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Cogeneration is classicly thought of as a conservation technique. What is perhaps less appreciated is the fact that cogeneration is also a technique for the reduction of emissions. This is one of the benefits of a cogeneration system since less fuel is burned to produce electrical power and process heat than in isolated powerplants or furnaces. Despite these benefits, there is concern that if cogeneration becomes widespread in the US on the scarce fuels of today (natural gas and light distilate petroleum) it could potentially displace the coal required by utility power generation and increases our imports of scarce fuels. If that can forseeably happen, and the US balance of payments to foreign countries were to increase, then very reasonable arguments can be made that cogeneration should not proceed without regard for the systems' potential for switching to fuels from far more abundant sources-like coal and coal-derived fuels. The author's position is not necessarily one of announcement of DOE policy but it is very much one of advocacy for cogeneration and the development of engine technology that can operate reliably and cleanly on fuels from coal at dispersed sites with the potential for utility ownership. Very direct benefits that this will permit are (1) the reduction of national consumption of scarce petroleum and natural gas to help the US balance of payments problem, (2) big increases in national coal production requirements, and (3) reduction in the amount of fuel required to make both electricity and process heat by factors ranging from 20 to 40% for the purposes of emission reductions on minimally processed coal-derived fuels, (4) keeping the cost for fuel burned in an operation from rising due to increased costs/BTU on coal-derived fuels and (5) dispersed power generation should reduce national vulnerbility to disaster of one form or another.

To give the reader some indication of how large the opportunity is for coal in cogeneration systems to meet the country's growing electrical and heat demands, refer to Figure 1. This shows a current and projected schematic of how energy is used in our two stationary sectors (commerical/residential and industrial) and how it is supplied by the purchase of fuel and the purchase of electricity from a utility company. In the year 2000, a projection of how heat and electrical requirements might be met with and without cogeneration is shown. Cogeneration is shown in the schematic to be used to meet national electricity growth requirements of nearly 8 quads electric between 1975 and 2000, with some recovered on-site waste engine heat being used to displace fuel that would otherwise be burned for process heat in these two sectors. While the overall national energy savings are only 5.3 quads/year, the new market for fuel burned in engines in cogeneration systems in this upper bound scenario is 25.3 quads/year. If heat engines and fuels from coal can be developed to meet this market and it's constraints (technical, environmental and cost) then this can be considered as a market for coal rather than scarce fuels. Note that this 25.3 quad/year market by 2000 is in addition to the current 20.2 quad/year fuel requirement of utilities.

The Opportunities for Coal Cogeneration in the New Market - Year 2000

No Cogeneration

1975

$20.2Q_H \rightarrow$ Utility

$4.0Q_E$

C/R $\leftarrow 12.6Q_E$

Industry $\leftarrow 2.6Q_E$

$21.0Q_H$

Total Fuel Used = $53.8Q_H$

No Cogeneration

2000

$43.2Q_H \rightarrow$ Utility

$7.5Q_E$

C/R $\leftarrow 13.3Q_H$

Industry $\leftarrow 36.4Q_H$

$6.8Q_E$

To[tal] Fue[l] Us[ed =] 92

With Cogeneration

2000

$11.5Q_H \rightarrow$ C/R Site

$3.4Q_{WH}$

$3.5Q_E$

C/R

$20.2Q_H \rightarrow$ Utility

$4.0Q_E$

$2.6Q_E$

$13.8Q_H \rightarrow$ Industry Site

$4.2Q_E$

Industry $\leftarrow 9.9Q_H$

$\leftarrow 32.2Q_H$

$4.2Q_{WH}$

Tot[al] Fue[l] Use[d] **87.**

New Opp[ortunities] for Cog[eneration] C/R Ind[ustry]
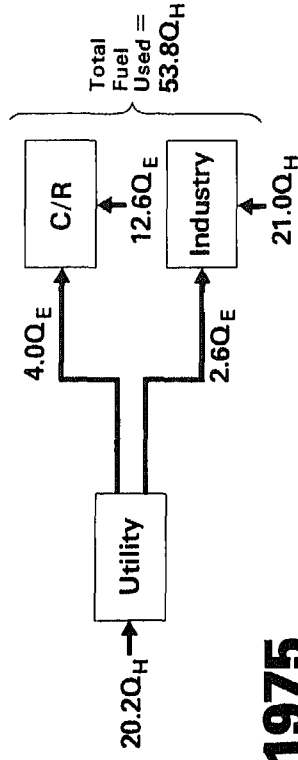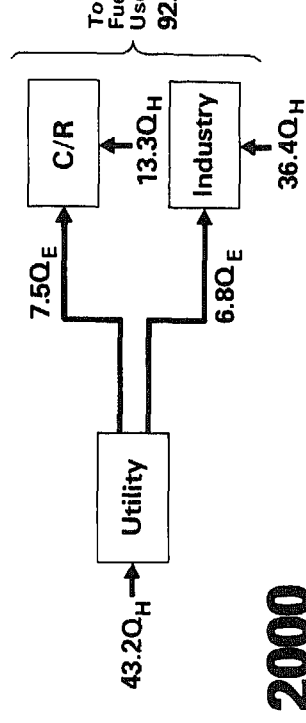
Symbols and Notes

Q_H = Quads Fuel Burned/Year

Q_{WH} = Quads Waste Heat Recovered in Cogen/Year

Q_E = Quads Electricity Made/Year

- 33 = Utility Electric Generation Efficiency
- 30 = Cogen Site Electric Generation Efficiency
- 60 = Total Cogen Cite Site Conversion Efficiency

Figure 1

79 - 00
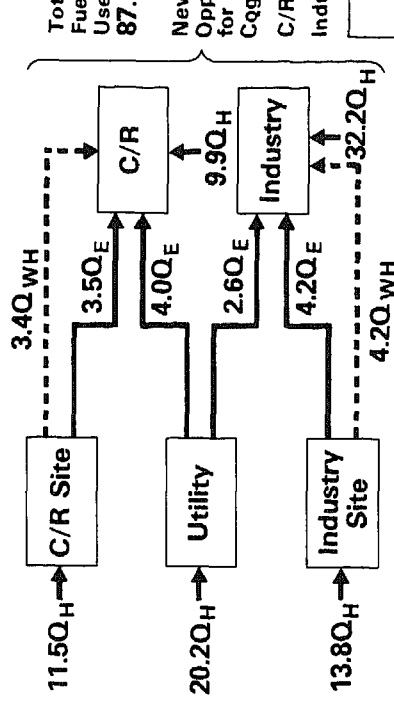
Figure 2.

Gas Turbine - HRSG Cogeneration Characteristics

·············· Air Cooled 1750 F PR = 10

▬ ■ ▬ ■ Air Cooled 2200 F PR = 12

▬▬▬ Water Cooled 2800 F PR = 16

Power or Heat/Fuel Ratios

C → HRSG POWER → STACK, HT

T SOURCE (°F) = T STACK

(axis: 0, 200, 400, 600, 800, 1000, 1200, 1400)

(y axis: 0, 0.2, 0.4, 0.6, 0.8, 1.0)

Ht

Pwr

Fuel Saved/ Fuel Burned

T SOURCE (°F) = T STACK

(axis: 0, 200, 400, 600, 800, 1000)

(y axis: 0, 0.2, 0.4, 0.6, 0.8, 1.0)

79
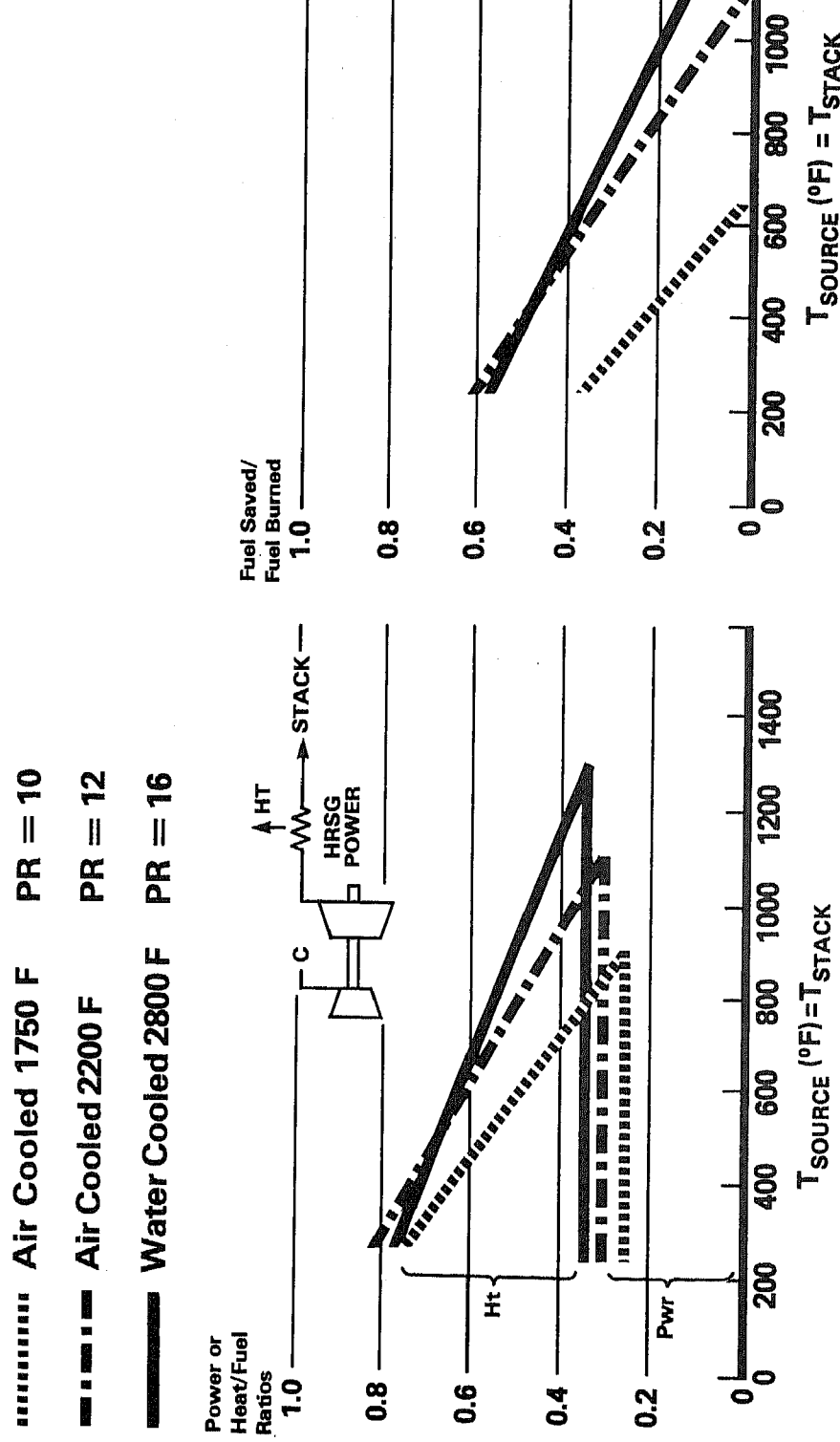
this fuel can be overcome-which is discussed next.

A very major technical barrier confronting the successful substitution of coal for scarce fuels is the fact the emissions from the combustion of coal derived fuels can be high enough to be considered unhealthy. The two most obvious solutions in engines are to (1) clean up the fuel to remove the polutants or (2) to develop engine technology to either burn more cleanly or clean up the exhaust products. A third solution, which is not quite so obvious is also applicable in reducing emissions. This third solution is cogeneration - the simultaneous generation of electrical or shaft power and process heat. The technical key to understanding how cogeneration can reduce emissions lies in understanding that in a "topping" type cogeneration system, the waste heat from a powerplant is used to make process heat instead of firing up an isolated furnace. The emission reduction comes from the industrial or commercial/residential furnace that is no longer lit. These 2 sectors now consume about 7 quads of electricity and 34 quads of fuel for heat, mostly in isolated non-cogenerated installations. In the future these requirements may be even greater and come to us at a time when it would be most desirable to meet these requirements using our most abundant fuel - coal. Means to do this job without sacrificing our environment however, are badly needed. Within these constraints it appears that cogeneration can be one of the most promising ways to make the combustion of coal acceptable for both power and process heat generation. The solution which this paper offers, cogeneration, not only reduces emissions it also is highly fuel efficient and can provide a market for the more economic, minimally processed coal-derived fuels. Some of the technical reasons why coal-derived fuels are not being used this way today even on a trial basis, are that (1) the best* of today's engines for cogeneration (diesels and gas turbines) can have severe operating problems on the impurities in these fuels. (2) even the emission reductions possible through only cogeneration are not enough to meet proposed EPA engine standards and (3) critical technologies for the balance of the coal cogeneration plant beyond the engine have not been investigated enough to know what their problems and solutions are. If these problems can be solved, there is still some barrier potential for industrial or commercial/residential cogeneration that can be anticipated if the environmental standards are based upon emissions per BTU input rather than emissions per usefull BTU output. In a cogeneration system, the usefull output can be on the order of 3 times higher than that of an isolated non-cogenerated powerplant with no increase in site emissions, despite the very large increase in usefull energy conversion. It seems very reasonable to the author that an environmental credit should be given for this added capability in BTU or equivalent KWHR that cogeneration can provide.

The following develops the rationale for these claims of emission reduction and increased useful output. Refer to Figures 2 to 5. Figure 2 from Reference 1 shows a candidate open cycle gas turbine cogeneration scheme making both electricity from a shaft driven generator and low temperature

*1) Best here means highest power/heat ratio.

Figure 3.

Effect of Cogeneration Upon Emissions

Isolated Power and Process Heat Production (No Cogeneration)

Power

230 PPM NOX
Exhaust
(0.7Lbs/10^6BTU)

$\eta_t = 0.30$

Engine

Gen | 1KW$_E$

Fuel 0.7% FBN

11500 BTU/KWHR

Process Heat

Water

Low Pressure Steam Boiler

Steam
h = 6325 $\frac{BTU}{HR}$

$\eta_t = 0.85$

230 PPM NOX

$\boxed{\frac{0.30 \text{ Lbs NOX}}{10^6 \text{ BTU}}}$ Exhaust

Fuel 0.7%FBN

7441 BTU/HR

$= .002232 \frac{Lbs}{HR}_H$

$\boxed{\text{Isolated Lbs NOX/HR}} = .007527 \frac{Lbs}{HR}_E + .002232 \frac{Lbs}{HR}_H = \boxed{.00976 \frac{Lbs}{HR}}$

Integrated Power and Process Heat Production (Cogeneration)

230 PPM NOX
Exhaust

Water Steam $\Delta h = 6325$ BTU/HR

Engine

Gen | 1KW$_E$

Fuel

11500 BTU/KWHR

$\eta_t = .85 = \frac{3412 \text{ BTU}_E + 6325 \text{ BTU}_H}{11500 \text{ BTU}_{Fuel}} = \frac{9737}{11500}$

$\boxed{\text{Cogenerated Lbs NOX/HR}} = \boxed{.007527}$

SN790344

Figure 4.

Taking Credit For Cogeneration Benefits
On .7% FBN Coal Liquid

1. If All The Credits Are Given To The Engine: Useful Output Almost Triples!

   $$\frac{\text{Engine Emissions/Output - Isolated}}{\text{Engine Emissions/Output - Cogen}} = \frac{.00753/3412}{.00753/9737} = 2.85 \quad \text{Emissions Slashed By Over 20\%!!}$$

2. If All The Credits Are Given To The Cogen System: Emissions Slashed By Over 20%!!

   $$\frac{\text{Total Plant NOX - Cogen}}{\text{Total Plant NOX - Isolated}} = \frac{.00753}{.00976} = .77 \quad \text{Emits Like FBN}$$

   Isolated Equivalency   Was Only .3%!

   Engine - 230 ppm NOX x .77 = 177 ppm   Saves $ .10 to

   Boiler - $\frac{.30 \text{ lbs NOX}}{10^6 \text{ BTU Input}}$ x .77 = $\frac{.23 \text{ lbs NOX}}{10^6 \text{ BTU}}$ $ .80/10^6 BTU!

   Better Than EPA Desired Standard!!!

the boiler which does not have to be fired to make the steam since this now comes from the cogeneration system.

For a direct comparison of emission and fuel reductions between isolated and cogenerated power and process heat generation on coal-derived fuels, see Figure 3. This figure shows an isolated boiler making low pressure process steam and an isolated gas turbine making electrical power. For illustration and comparison purposes, the boiler is sized to put as many BTU/HR into steam as the cogenerated gas turbine does. To make the case scaleable, the electricity generated is 1 KW. In the illustration, the fuel used is an undefined coal-derived liquid containing .7% fuel bound nitrogen with both the boiler and the turbine using the same fuel. The fuel bound nitrogen level selected corresponds closely to that of fuels that were burned in a gas turbine combustor (Ref. 2) and in a utility furnace that had originally been sized for coal (Ref. 3 and 4). The engine and boiler emissions of NOX shown in Figure 3 are therefore, based upon actual coal-derived liquid fuel burns in production equipment. No speculation is made in this paper as to whether or not these values are going to be typical, but the ones shown do reflect what was measured. Cogeneration is shown to reduce the system emissions of NOX by 23% owing to the elimination of the boiler, its fuel demand and the emissions from that fuel. This brings up a subtle but very important point, that any impact of cogeneration is due to the equipment it replaces. The boiler shown in the example only emitted .3 lbs $NO_x/10^6$ BTU fuel input. If, for whatever reason, that emission had been higher, say .7, as might occur on furnaces originally designed for natural gas or light distillate, then the lbs of NO_x/Hr would have risen from .00223 to .00521 for the boiler contribution. This would have raised total system emissions of NO_x/Hr from .00976 to .01274. Eliminating such a high emission boiler through cogeneration would reduce total emissions by 41%. The point is that the impact of cogeneration upon emissions is dependant upon what is being replaced.

Figure 4 shows some various aspects of how these emissions reductions might be credited for the user. Two methods are shown. The first method credits the emission reduction uniformly for all members of the system as a whole -rather than to one component of it. In this form of acreditation, the total NOX reduction for power and process heat production is 23%. This means that the site of the cogeneration system is only making 77% of the NOX that would be formed by an isolated gas turbine plus an isolated boiler. For the boiler this would be equivalent to an isolated unit emitting only .23 lbs $NO_x/10^6$ BTU, which is considerably better than EPA standards. For the gas turbine, a 23% reduction in NOX would be equivalent to reducing its

[*1)] Ref. 1 also shows a combined cycle gas turbine (42% efficiency) with its waste steam going directly to process heat with 70% cogeneration system efficiency in the 300^o - 400^oF stack temperature range.

when coal-derived fuels are used that are high in fuel bound nitrogen. It is worth noting that based upon Ref. 2's information, a reduction in NOX from 230 ppm to 177 ppm is equivalent to operating an isolated engine on .3% FBN fuel rather than .7% FBN. In a system that combined both cogeneration _and_ an advanced low NOX combustor gas turbine, the minimally processed .7% FBN fuel might have been used and the additional fuel cleanup cost avoided. Over a 5 year period, operating 65% of the time (28470 hrs), a fuel cost savings (by being able to use .7% FBN instead of .3% FBN fuel) of $.60/MBTU (Ref. 5) would result in a savings of $196.40/KW. Since this figure is higher than the installed price of a gas turbine, it suggests that just the savings in not having to do additional fuel cleanup would pay for the powerplant in 4-5 years.

Compared to the isolated system, the cogeneration system only consumes 60% as much fuel for the same output. One way of interpretting this is that the cogeneration system could possibly more easily afford a substantial increase in fuel price if it were to rise from $3/MBTU (today's price) up to $5/MBTU (a possible future price).

In summary, the substantial impacts of cogeneration for the case given were:

1) An actual fuel consumption reduction of 40%, and an attendant NOX reduction of 23 to 41%, depending upon the performance of the replaced boiler.

2) An ability to burn minimally processed coal-derived fuels, rather than the more highly processed varieties with a savings over a 4 to 5 year period big enough to pay for the installed capital equipment price of even advanced gas turbine powerplants.

3) An ability to tolerate a rise in fuel price from $3/MBTU up to $5/MBTU - if the fuel is used in a cogeneration system - with no increase in price of either electricity or process heat to the customer because of a fuel price increase.

The second method gives all the credit to the engine due to the fact that although it's emissions do not change, its output in terms of useful BTU's goes up by a factor of 2.8. This output per emissions factor is simply the ratio of engine thermal efficiency with and without cogeneration. Usually this does not mean that emissions are reduced by a factor of 2.8. There are certain cases however, where it does mean exactly that. These are the cases where heat can be supplied in lieu of electricity for direct element heating, particularly where this electricity comes from peaking gas turbines. For the case given, if the cogenerated low pressure steam (or hot water) could replace electricity made by isolated gas turbines like the one in the example, the NOX produced to make the same useful output (9737 BTU) would be .00753 lbs, rather than (9737/3412)x .00753 or .0213 lbs, which is lower

The Impact of Advanced Cogeneration on Emissions

Figure 5.

Range for Conventional Engines Making Only Electrical Power

Range for Advanced Engines in Advanced Cogeneration Making **Both**

- Electrical Power
- Process Heat

Emissions/Useful Output - Isolated Engine/Emissions/ Useful Output - 100% Energy Conversion

Efficiency of Fossil Fuel Utilization

0   0.2   0.4   0.6   0.8   1.0
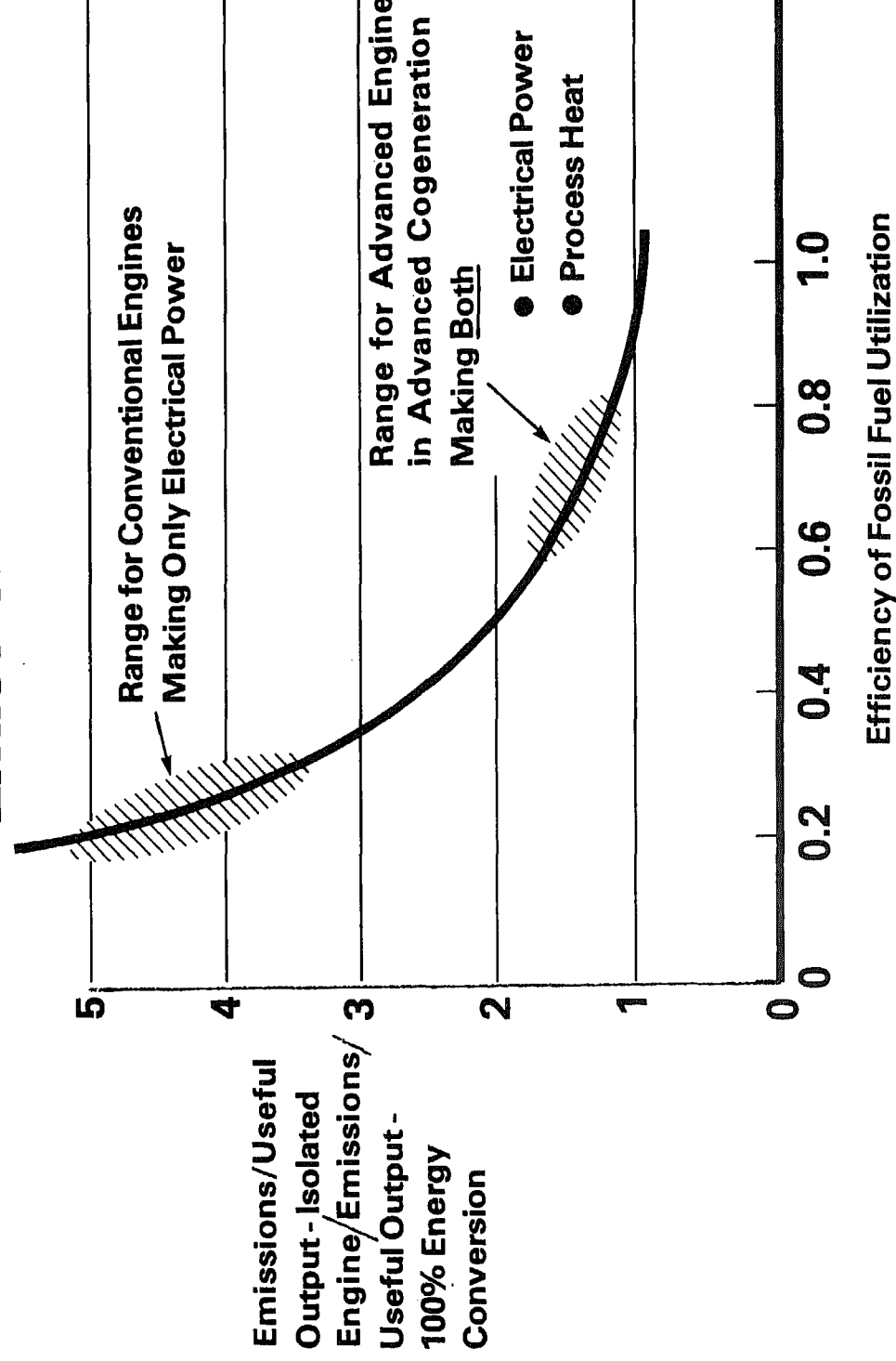
discussion of their individual behavior in cogeneration systems too lengthy for this paper. However, some gross definition of the impact of cogeneration upon the emissions of the cycles is still desirable. An attempt to show this is given in Figure 5.

Figure 5 shows the ratio of emissions/output for isolated powerplants to emissions/output for 100% energy conversion plotted versus installed thermal efficiency. This curve is a direct presentation of the second method of acreditation given previously in which all the credit for the conversion to additional useful energy is given to the engine. The message from the figure is that cogeneration can boost the useful power and heat output of engines by factors as high as 3. While this does not reduce the site emission level for power generation, it does reduce the need for combustion of a fuel elsewhere to get the extra output now being made through cogeneration. In the example given, the ordinate value for the isolated gas turbine making only electrical power is 3.33 and the value for the cogenerated gas turbine is 1.18. The ratio of those two values is 2.8 which means the output of the cogenerated system is 2.8 times as much as the isolated system with no increase in fuel consumption or emissions.

The preceeding has given a reasonable indication that cogeneration can have a large beneficial effect not only in reducing emissions but also in making large financial savings in the life cycle of power and heat generation on minimally processed coal-derived fuels. Cogeneration seems to be a means of overcoming many of the technical, economic and environmental problems associated with coal. In recognition of such powerful leverage, in FY 1978 and FY 1979, the Fossil Energy Group of Energy Technology at DOE has established a series of major programs intended to (1) identify the major opportunities for cogeneration on coal and (2) to develop the technology in engines to permit them to operate reliably and cleanly on the lower cost minimally processed coal-derived liquid fuels.

In the first area, the 1985-2000 time frame is being addressed with major emphasis on obtaining optimum matches between engines of all types and the electrical and process heat requirements of 6 major industries and a commercial/residential mix. The industrial program now constitutes 2 major parallel study contracts (GE and UTC) let through NASA, Lewis Research Center. They are investigating the technical merits of diesel, stirlings, gas turbines, steam turbines, fuel cells, thermionics, bottoming cycles and energy storage for cogenerating the chemical, refining, paper, metals, stone/clay/glass/cement, and food industries with extensive applications of coal-derived fuels being sought. This program is called the "Cogeneration Technology Alternatives Study" (CTAS) and the contracts end in March 1979. The commercial/residential study is termed "Total Energy Technology Alternatives Study" (TETAS) which is being conducted in-house at Argonne National Laboratory. In this study, ANL is trying to find optimum matches between most of the topping cycles and heat pumps of CTAS and the power/heat requirements of a commercial/residential mix - shopping center, townhouses,

on coal-fueled engines.

The one major assumption of the above studies is that they, by definition, presuppose that engines can operate at least reliably and possibly cleanly on coal-derived fuels. With the exception of the steam turbine, this is not necessarily true today. Fortunately, however, Fossil Energy in DOE has made major strides in establishing engine programs to provide the fuel flexibility capabilities that the studies assume exists. The major thrust of the programs are in diesels, gas turbines and Stirlings. The Stirling has the most fuel flexibility of all, because like the steam turbine it is externally fired which means its working fluid never comes into contact with the products of combustion. The Stirling's problem is that its major development for widespread commercialization was stopped around the turn of the 20th century due to the availability of cheap, clean, fuels suitable for internal combustion engines. Fossil Energy will have 2 small units built and scheduled for their first run in FY 1979. The conceptual design of a large unit will be started in FY 1979 with the first engine to test about 5 years later. The gas turbine can burn mostly any liquid or gas that is combustible, including coal-derived fuels. The gas turbine's problem on coal-derived fuels is that without additional processing of the fuel, many of these fuels contain traces of what is in coal - namely fuel bound nitrogen which produces high NOX levels, ash which may give turbine erosion problems and minute quantities of vanadium and alkali metals that give the turbine severe corrosion problems. The solutions to these problems seem to be the development of coatings and low-NOX combustor techniques. Two major DOE programs in these two technologies will be on multiple contract by January, 1979. With adequate funding, the programs will last about 5 years each and will be complete with demonstration in an engine(s). This work dovetails with complimentary development efforts on gas turbines for utility companies being performed through EPRI for baseload and intermediate capability on residual oils and coal-derived fuels. Of the three power-plant types mentioned, the one which seems closest today to a multi-fuel capability is the stationary diesel. This is based upon the fact that under DOE sponsorship several coal-derived liquid fuels have been run in a large diesel engine with less than a 10% increase in NOX as compared to light distillate operation. DOE plans to initiate a program in FY 1979 that will more fully asses a range of stationary diesel sizes on coal-derived liquid fuels. The primary things to be learned relate to emissions, corrosion, erosion, deposition, wear and what it takes to get fuels with very low cetane numbers to ignite.

The overall conclusion of this paper is that cogeneration offers a very powerful technique for the successful use of coal as a means of reducing oil imports, emissions, fuel costs and operating costs. The key technologies will require continued development in three major complimentary areas - coal-derived fuel processing, engines to burn these fuels cleanly and reliably and all other critical components needed to cogenerate besides engines and fuels.

18 April 1978, GE, Energy Systems & Technology Division,
Schenectedy, NY 12345

2. Efforts performed in 1978 under "Combustors for Coal-Derived Liquids
   With High Bound Nitrogen," EPRI Contract RP 989-1, by Westinghouse
   Electric Corp., Lester PA 19113

3. Mr. Richard Corey, DOE/ET/FE, Oct. 1978, 20 Mass. Ave. N.W.,
   Washington, D.C. 20545

4. Mr. Don Teixeira, Oct. 1978, EPRI, 3412 Hillview Avenue, P.O. Box 10412,
   Palo Alto, CA 94303

5. "Economic Screening Evaluation of Upgrading Coal-Liquids to Turbine
   Fuels" AF-710, Technical Planning Study 76-666, Final Report
   March 1978, by Mobil Research and Development Corp., Billings Port
   Road, Paulsboro NJ 08066, EPRI Project RP 361-2

FOSSIL FUELS – ADVANCED METHODS I (LIQUIDS)

Chairman: William Peters

Co-Chairman: Fred Witmer

C. E. Schmidt and M. S. Edmunds
U.S. Department of Energy
Pittsburgh Energy Technology Center

A high resolution mass spectrometric (HRMS) screening technique developed
at the Pittsburgh Energy Technology Center (PETC) was used to screen
process streams from coal gasification and liquefaction for possible
hazardous compounds. The screening technique compares precise masses deter-
mined by high resolution mass spectrometry to those masses of chemical
formulas corresponding to selected hazardous and/or toxic compounds. The
hazardous compound list employed in the HRMS screening program is comprised
of nearly 700 hazardous compounds from OSHA, EPA, NIOSH, ACGIH, and NAS lists.
HRMS screening data was obtained on coal gasification tars and all the major
process streams from the PETC 400 lb/day liquefaction PDU. Liquefaction
product made with an added catalyst was found to contain fewer possible
hazardous compounds than product made without added catalyst as determined
by the HRMS screening technique. Concentrations of specific compounds in
process waters from both gasification and liquefaction processes were
determined by direct injection gas chromatography.

METHODOLOGY DEVELOPMENT FOR THE DETERMINATION OF POLYCYCLIC
AROMATIC HYDROCARBONS (PAH) IN FUGITIVE EMISSIONS
FROM COAL LIQUEFACTION PROCESSES

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U.S. Department of Energy
Pittsburgh Energy Technology Center

and

Milton L. Lee and Daniel L. Vassilaros

Bringham Young University

The objective of this project is to develop a method for the quantitative
collection and analysis of polycyclic aromatic hydrocarbons (PAH) in fugitive
emissions from coal liquefaction processes. Coal liquefaction products and

Toward this objective, it has been shown that PAH can be quantitatively sampled from ambient air, and the collected sample can be quantitatively recovered from the collection media by solvent extraction, using n-pentane. Further, dilute solutions of PAH in n-pentane can be concentrated by solvent removal using a Kuderna-Danish evaporative concentrator, with minimal sample losses. The chromatographic resolution of complex mixtures of PAH expected to be present in fugitive emissions from coal liquefaction processes is best attained using high resolution glass capillary-gas chromatography. The gas chromatographic retention characteristics of over 200 PAH have been determined, and a new gas chromatographic retention index system unique for PAH has been developed. The PAH retention index system provides for the tentative identification of numerous PAH in these complex mixtures. Positive identification is obtained when the retention indices are combined with mass spectral data on the same chromatographic peaks. The use of the new PAH retention index system will be demonstrated by the analysis of an aromatic fraction from a coal liquefaction product.

INTEGRATED COMPLIANCE AND CONTROL TECHNOLOGY RESEARCH ACTIVITIES
FOR IN SITU FOSSIL FUEL PROCESSING EXPERIMENTS

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U.S. Department of Energy
Laramie Energy Technology Center

Fossil fuel processing research facilities must comply with Federal and state regulatory standards. In addition, the experimental sites provide research opportunities to evaluate control needs and then design and demonstrate control measures as each technology approaches commercialization. This paper will summarize the regulatory compliance and control technology activities and illustrate their integration as pertaining to field in situ recovery experiments for oil shale.

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Battelle Pacific Northwest Laboratories

Wastewater disposal is an important element to be considered in evaluating the environmental impact of the developing shale oil industry. Wastewater can be generated by a number of different sources within a shale oil recovery facility, depending on the type of recovery system used, the location, and the type of oil shale processed. The pollution potential of the wastewater may be very high as in the case of retort water or it may be low as in the case of some minewaters. Above-ground retorts may reuse all wastewater streams generated within the mining and processing facilities to moisten spent shale for compacting in the dumping areas. Moisturizing spent shale is not performed at in situ operations; therefore, substantial wastewater discharges are anticipated at their installations. In situ retorting produces water in approximately the same volume as the oil produced, consequently a 100,000 barrel per day facility would generate about 4 million gallons of retort water each day for disposal.

Studies have been completed on the evaluation of land disposal and underground injection as disposal options for shale oil wastewaters. Land disposal is the application of wastewater at the soil/air interface to utilize natural chemical and physical reactions for purifying the wastewater. Underground injection makes use of deep confined aquifers or isolated geological zones for discharge of wastewaters. The results of this investigation indicate that both the wastewater characteristics and the climate of the oil shale regions of Colorado, Utah, and Wyoming are not favorable for land disposal of retort water. Underground injection is a viable disposal option for retort water where geological conditions are favorable; however, regulatory restraints are expected to limit the use of this option.

Studies are currently in progress on benchscale evaluations of treatment technology for retort water and mine water. Conventional biological treatment appears to be adversely affected by toxicants in the retort water, however, preliminary results indicate that the addition of powdered activated carbon may overcome this problem. Several different methods have been investigated for removal of fluoride, boron, and alkalinity from minewaters. Ion exchange is a leading candidate for treatment of minewaters.

M. M. Moody and C. J. Sisemore
Lawrence Livermore Laboratory

Burned out oil shale retorts need to be stabilized to prevent subsidence of the overburden and the ground surface; prevent gas leakage; maximize resource utilization; and provide subsurface disposal of spent shale that has been retorted on the surface and minimize ground water contamination.

We believe that in order to stabilize the retorts, the following strategy should be followed.

(1) Characterize the components of the retort such as overburden and pillar strength: temperature effect on strength; retort and pillar permeability; and rubble behavior during and after retorting.

(2) Develop slurry that can accommodate a maximum amount of spent shale and low quality water.

(3) Investigate techniques for emplacing the grout and sealing the retorts.

(4) Develop a retort cooling process whereby sensible heat can be recovered and the residual rubble will have properties amenable to grouting.

(5) Prepare a full scale field test program to evaluate the optimum combination of cooling procedures, grout and emplacement techniques.

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U. S. Department of Energy
Bartlesville Energy Technology Center

The injection of wastes into deep underground formations is the most economical method for disposal of liquid wastes that are not amenable to surface treatment. Operating costs are lower for pretreatment and subsurface disposal than for surface treatment systems, and plant area requirements are less. Chemical treatment is minimal, and generally the only physical treatment required for underground injection is filtration. This report presents a broad view of modern industrial underground waste injection systems and their operations. The types of wastes being injected and the major features of equipment, geologic formations, and well operation are described.

The petroleum industry has been injecting fluids into subsurface formations for many years; therefore, many of the techniques and much of the equipment for handling industrial liquid wastes are already available for industrial waste disposal or can be modified to meet the specialized requirements. The techniques for drilling and completing the disposal wells have been perfected, and the equipment to do it is in service. Similarly, the behavior of fluid flow through porous rocks and unconsolidated sand has been investigated; therefore, many of the theories and equations describing the fluid distributions have been proved. Modification may, however, be needed to make them applicable to waste injection systems and to describe the radial chromatographic properties of the injected wastes constituents.

A subsurface disposal system can be successful only if a porous, permeable, formation of wide areal extent is available at sufficient depth to ensure safety in storage and retension of the injected fluids. The wastes usually are treated for solids removal and compatibility with the formation. An impermeable zone, such as shale or evaporite, must overlie the injection horizon to prevent vertical migration of the waste or displaced formation brines into low-salinity aquifers above the disposal zone.

General principles of design and construction are applicable to all subsurface injection systems; therefore, this report is presented in three parts. First the general technology of subsurface disposal systems is presented with notations on cost; second, the general geology of the United States is discussed with reference to subsurface waste disposal; and third, detailed discussions are presented on disposal systems that illustrate particular design and operating features.

Paper not submitted for publication in Proceedings.

SCREENING COAL GASIFICATION AND LIQUEFACTION PROCESS
STREAMS FOR POSSIBLE HAZARDOUS COMPOUNDS

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ABSTRACT

Fossil fuel processing research facilities must comply with federal and state regulatory standards. This paper summarizes the research effort in effect at the Laramie Energy Technology Center and regulatory requirements pertaining to control technology for process waters associated with in situ oil shale processing. In addition, the experimental sites provide control needs and then design and demonstrate control measures as each technology approaches commercialization.

INTRODUCTION

The Laramie Energy Technology Center (LETC) is primarily responsible for the development of in situ recovery technologies related to such alternate fossil fuel resources as oil shale, coal, and tar sands. Advancing in situ technologies to commercial practicability involves a progression of field experiments through which the engineering, environmental, and economic issues can be explored and resolved. In 1977, legislation was passed requiring federal facilities to comply with federal, state, and local regulations and standards when conducting field experiments. Environmental efforts at LETC address compliance requirements at field sites and generate information that can be transferred to industry and environmental regulatory agencies as in situ technologies approach commercialization. This paper will illustrate, through specific examples, the development of control technology in conjunction with compliance requirements.

BACKGROUND

The goals of the environmental effort at LETC are (1) to identify, quantify, assess, and reduce to within acceptable levels any adverse environmental impact that may result from in situ fossil fuel processing field experiments conducted by LETC and (2) to accelerate the acquisition and application of environmental and compliance data related to in situ fossil fuel processing so as to move the technologies towards commercialization.

The development of in situ processing technology is primarily accomplished through a schedule of field experiments. Environmental research
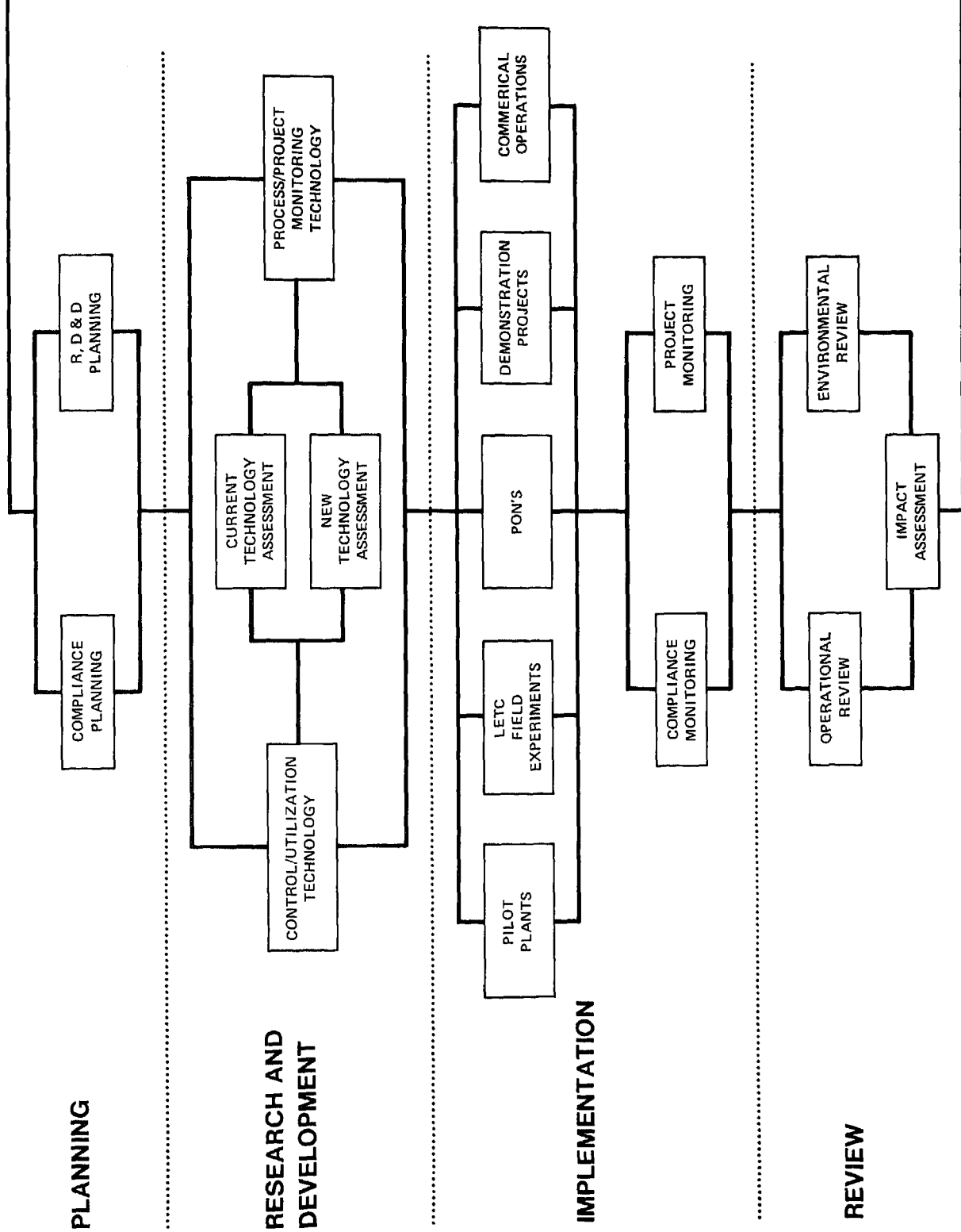
PLANNING

RESEARCH AND DEVELOPMENT

IMPLEMENTATION

REVIEW

FIGURE 1. LETC ENVIRONMENTAL ACTIVITIES

mental areas are achieved. Therefore, the LETC approach is based on the coordinated and integrated use of every field experiment to further both process and environmental RD&D efforts. In many instances, environmental work is conducted outside of the field activity (e.g., laboratory, review, or assessment work). Nevertheless, under the LETC approach such work is either derived from or oriented towards a field activity.

The general approach for the environmental activity at LETC is shown in Figure 1. This diagram illustrates the primary areas (in boxes) associated with various stages of environmental activity as it progresses from planning, through R&D, to implementation, and review. These stages are iterated to account for the changing implementation focus as it progresses from pilot plant facilities to commercial operations. Within this framework, all subjects of environmental concern are addressed, including potential air, water, land, ecologic, socioeconomic, occupational, and aesthetic impacts.

It should be evident from Figure 1 that the scope of environmental work at LETC is quite broad. LETC in house field activities are also numerous, with projects currently in progress near Bonanza, Utah and Rock Springs, Wyoming (oil shale), Hanna, Wyoming (underground coal gasification), and Vernal, Utah (tar sands). To more effectively illustrate the inter-relationship of compliance activities related to field projects with other environmental efforts, specific subjects have been selected; namely, the Rock Springs experimental in situ oil shale facility and control technology for in situ oil shale process waters. Water-related problems are pertinent to all in situ technologies from both regulatory and research points of view. Thus, this discussion will address a significant subject in some detail, while at the same time it will serve to illustrate the LETC approach of coordinating and integrating process and environmental research at the field level for all technologies. A summary of environmental research conducted by LETC for in situ oil shale processing, which includes reference to process data, has recently been published (1).

DISCUSSION OF CONTROL TECHNOLOGY FOR PROCESS WATERS

In this paper the term "process water" refers to all contaminated waters originating in conjunction with the in situ oil shale process. Process waters are derived from the following primary sources: (a) water formed as a byproduct of the combustion of organic matter in oil shale, (b) water released by dehydration of oil shale minerals, and (c) native groundwater associated with or intruding into the retorting zone (1). As a result of their intimate association with the retorting process, these waters become heavily laden with both organic and inorganic constituents. A summary of water quality parameters for process waters derived from both simulated and true in situ retorts is presented in Table 1 (2). This table indicates that process waters characteristically are alkaline and contain high levels of solids and dissolved organics. Principal inorganic constituents include ammonia, ammonium, bicarbonate, carbonate, magnesium, sodium, and various sulfur species. The organic constituents are primarily polar in nature, with carboxylic acids

Parameter	Simulated In Situ Retorts[b] Range		Average	(Omega-9 Water Composite) Best Value[c]
Alkalinity, total (mg/ℓ CaCO$_3$)	18,200	110,900		16,200 ± 480
Aluminum	0.041	16.6		<0.03 · 19.1
Arsenic	0.46	10	1.8	1.0 ± 0.2
Barium	0.002	0.47	0.07	0.71 ± 0.33
Beryllium	<0.001	<0.001		<0.006
Bicarbonate, mg/ℓ HCO$_3^-$	4,200	73,640		15,940
Biochemical oxygen demand, 5-day	350	5,500		740
Bromine	<0.001	1.94	0.082	2.4 ± .4
Cadmium	<0.001	0.005		0.0016 ± 0.0008
Calcium	0.0	94	7.6	12 ± 4
Carbon, inorganic, mg-C/ℓ	1960	19,200	7,500	3340 ± 390
Carbon, organic, mg-C/ℓ	2,200	19,000	4,700	1003 ± 192
Carbonate, mg-CO$_3^-$/ℓ	0.0	15,210		500
Chemical oxygen demand	8,500	43,000	18,500	8100 ± 5700
Chlorine	0.007	1910		824 ± 61
Chromium	0.009	0.08	0.015	0.02 ± 4%
Cobalt	0.002	0.65	0.12	0.030 ± 0.012
Conductivity, μmhos/cm	15,100	193,000	31,000	20,400 ± 3840
Copper	0.003	160	0.019	0.10 ± 0.04
Fluoride	0.1	270		60 ± 9
Hardness	20	1,500	88	110
Iodine	<0.001	1.3		0.59 ± 0.30
Iron	0.091	77	7.6	1.2 ± 0.3
Lead	0.002	0.83		0.0045 · 0.02
Lithium	<0.001	7.1	0.70	0.18 · 0.8
Magnesium	3.2	350	22	20 ± 6
Manganese	0.001	0.39	0.099	0.09 ± 0.04
Mercury	<0.001	0.39		0.0003 · 0.021
Molybdenum	0.033	1.2		0.60 ± 0.07
Nickel	0.014	2.6		0.06 ± 0.02
Nitrogen, ammonia, mg-NH$_3$-N/ℓ	1,700	13,200	7,000	3795 ± 390
Nitrogen, ammonium, mg-NH$_4^+$-N/ℓ	930	24,450	10,000	3470 ± 830
Nitrogen, nitrate, mg-NO$_3^-$-N/ℓ	1.4	8.7		0.17
Nitrogen, organic, mg-N/ℓ	73.3	1510		148 · 630
Nitrogen, Kjeldahl, mg-N/ℓ	6,600	19,500		3420 ± 420
Oil and grease	3,800	3,800		580
pH	8.1	9.4	8.7	8.65 ± 0.26
Phenols	2.2	169		60 ± 30
Phosphorus	0.23	19.0	1.25	3.2 ± 2.6
Potassium	8	120	37	47 ± 9
Selenium	<0.001	1.7		0.21 ± 0.11
Silver	<0.001	0.23		0.003 ± 0.001
Sodium	45	1600	320	4333 ± 244
Solids, dissolved	1,750	24,500	6,800	14,210 ± 193
Solids, total	6,350	121,000		14,210 ± 120
Solids, volatile	2,070	119,300		
Sulfur, sulfate, mg-SO$_4^-$/ℓ	42	2,200	1,400	1990 ± 250
Sulfur, sulfide, mg-S$^-$/ℓ	0.0	156		0.0
Sulfur, total, mg-S/ℓ	14	2320		2300
Uranium	0.018	93		0.55 ± 0.07
Vanadium	0.004	>190	0.27	0.12 ± 0.01
Zinc	0.020	15.1	0.28	0.31 ± 0.04

[a] Selected values taken from reference (2). *This reference should be referred to for discussions pertinent to each value given above.*

[b] The range given is based on the analysis of up to 18 different waters obtained from 4 simulated in situ oil shale retorts. An average value is given only if 15 or more waters were available.

[c] Best values determined by a statistical technique in the analysis of results obtained from a multilaboratory, multimethod survey of the Omega-9 sample.

field in situ experiments.

The quantity of process waters produced during in situ oil shale processing is dependent upon several factors, including the mineral content of the oil shale, the volume of groundwater present or seeping into the retorting zone, the duration and areal extent of the burn, the amount of organic resource combusted during retorting, and the amount of injected water (1). The ratio of process water to oil produced at the surface during field experiments has been noted to vary from 0.4 to 22.2 (1). The minimum volume of surface-produced process water derived from in situ processing is estimated to be near the volume of oil produced (1). This minimum volume would amount to nearly 5,000 acre-feet of process water per year for every 100,000 barrels of shale oil produced per day.

The preceding discussion establishes that low quality process waters originating from the in situ process will have both a surface and a subsurface disposition, both of which pose potentials for environmental contact. The intrusion of groundwaters into retorted zones and their subsequent contamination is another source of possible subsurface disturbance. The goal of process water-related control technology research at LETC is to demonstrate, in conjunction with all applicable compliance criteria, techniques for the effective control and, where practical, utilization of both surface- and subsurface-released aqueous effluents so as to mitigate any undesirable environmental effects. The achievement of this goal is prerequisite to the establishment of a full-scale, commercial in situ oil shale processing industry. Figure 2 illustrates the steps required and the approach being followed by LETC to achieve the goal of control technology for in situ process waters. This figure is largely self-explanatory, and the remainder of this section will be devoted to a discussion of some of the concepts illustrated.[1]

It should first be noted that two primary efforts are being conducted simultaneously; namely, the control of process waters associated with surface and subsurface release. Although not diagrammatically illustrated in Figure 2, many of the work elements provide data and results common to both pursuits (e.g., site monitoring, process water balance determinations, and possible utilization of surface produced waters for subsurface applications, such as steam injection). The determination of appropriate or necessary control, treatment, or utilization options for water released at either the surface or in the subsurface logically precedes systems engineering design efforts. In this program, such a determination is based on two primary inputs. The first input is obtained from examining current or anticipated compliance requirements related to released process waters. The initiating role that compliance

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[1] Reference (1) provides key references to work published up to 1978 in the subject areas indicated. Subsequent citations or additional technical information may be obtained from the authors.
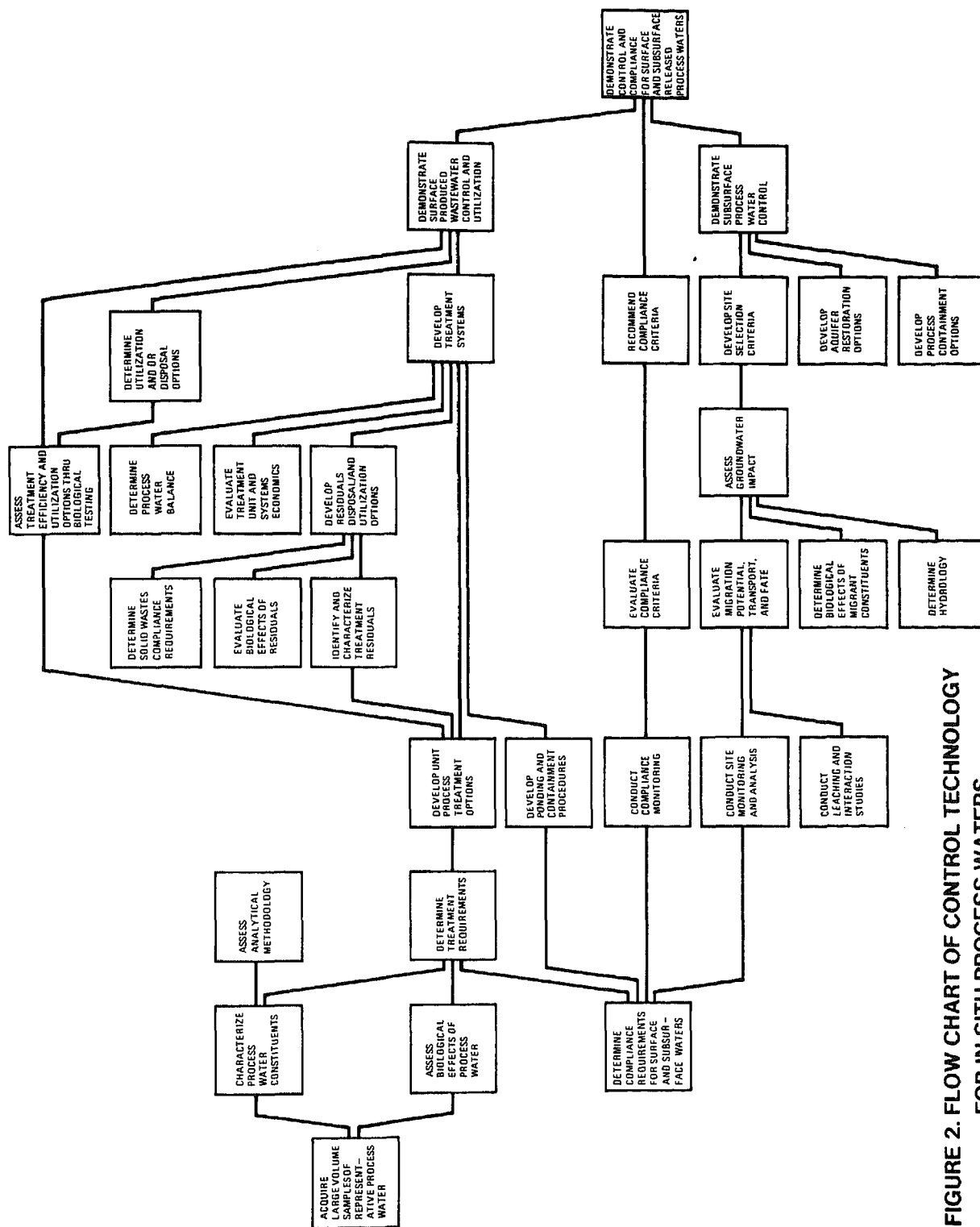
FIGURE 2. FLOW CHART OF CONTROL TECHNOLOGY FOR IN SITU PROCESS WATERS

current regulations certainly serve as a starting point for control technology design, there is scope for progressive improvement and refinement of these regulations as our knowledge of process water impacts and mitigation options increases.

The second primary input in determining control requirements and options is based on findings and recommendations from research specifically designed to identify impacts resulting from released process waters. Characterization of the constituents in process waters, assessment of the biological effects of process waters, and determination of the migration potential, transport, and fate of process water constituents through site monitoring and laboratory experiments all represent this type of research.

Considering the ever increasing demands on the limited water resources of the semi-arid oil shale-bearing regions of the West, water produced during in situ processing in itself should be considered as a potentially valuable commodity. The possible use of process waters for both on- and off-site purposes is therefore given considerable attention early in the development of unit and process train treatment systems. At this time the most probable uses for excess process waters are related to steam reinjection, site steam genera-tion, heat exchanger and cooling water, and land applications, such as for irrigation during revegetation and rehabilitation of sites. Economic considerations should include consideration of solute recovery from the process waters during treatment as a means of offsetting treatment costs.

An inevitable consequence of any treatment procedure is that a concentra-tion of residuals will be removed from the influent stream. The development of acceptable options for the disposal and/or use of such residuals is considered to be a fundamental part of the overall development of an acceptable treatment system. The multiplicity of potential uses and the rather unique compositional characteristics of process waters considerably limit the applicability of existing water treatment technologies to process water treatment needs. It is therefore necessary that a variety of treatment methodologies -- spanning primary, secondary, and tertiary treatment by physical, chemical, and biological means -- must be explored simultaneously to determine their capability for handling these type waters. There is currently a broad effort under way in this area (1). In the meantime, field experiments will continue to produce excess effluents. A temporary measure available now is to contain such waters until functioning treatment systems are in place. Also, evaporation ponds established at field sites offer excellent opportuni-ties to study ponding practices.

An assessment of the impact that subsurface released process waters and leachates from retorted zones may have on groundwater quality is an active research objective at field sites. Should groundwater quality changes be determined as profound and persistent, then the obvious mitigation procedure would be to select in situ processing sites where the hydrologic, strati-graphic, or other considerations would be such that groundwater disturbance or degradation would be prevented. However, this recourse would limit the amount of available resource. It is therefore necessary that other options for mitigating groundwater impacts be explored. Methods for the containment

The starting point, and the final proving ground, for process water control technology development is in the field environment. It is here that relevant water samples, containing all the variances imposed by the process, are obtained. It is in this environment that the dynamic factors (migration, bioavailability, ecological effects, utilization options) are at work. Thus, it is at these locations where the control technology must first be demonstrated.

DISCUSSION OF WATER-RELATED COMPLIANCE REQUIREMENTS

Now that some important dimensions of process water control technology have been discussed, it is necessary to examine the legal and regulatory structure within which such processes must function. This section will examine both Federal and Wyoming environmental laws and regulations that impinge upon the implementation of in situ processing technologies involving both surface and subsurface water.

Laws and regulations apply to air pollution, water pollution, land reclamation, toxic substances, solid waste, occupational safety, health, and many other aspects of in situ processing. As noted earlier, we will address environmental regulations as they apply to surface and subsurface water.

Surface Waters

The Federal Water Pollution Control Act (FWPCA) (3) established goals to eliminate discharge of pollutants into navigable waters by 1985 (4); to achieve interim goals of water quality which provides for the protection and propagation of fish, shellfish, and wildlife (5); and to prohibit discharge of toxic pollutants (6). In order to achieve these goals, industrial facilities can be regulated through three different mechanisms -- standards are established for maintenance of the quality of receiving waters; standards of performance can be established for specific classes of emission sources; and standards can be established for specific toxic pollutants.

Standards Based on Quality of Receiving Water

The FWPCA bases effluent limitations on water quality of the receiving water:

> Whenever. . . discharges of pollutants from a point source
> or group of point sources . . . would interfere with the
> attainment or maintenance of that water quality in a specific
> portion of the navigable waters which shall assure protection
> and propagation of a balanced population of shellfish, fish,
> and wildlife, and allow recreational activities in and on the
> water, effluent limitations (including alternative effluent
> control strategies) for such point source or sources shall
> be established which can reasonably be expected to contri-
> bute to the attainment or maintenance of such water quality (7).

Standards of Performance for New Effluent or Emission Sources.

In addition to effluent regulations based upon the quality of receiving waters, the FWPCA orders EPA to establish "National Standards of Performance" for new effluent or emission sources in 27 different industries. "Standards of Performance" are defined as:

> ...a standard for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator of EPA determines to be achievable through the application of the best available demonstrated control technology, process, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants (8).

In establishing standards of performance, the EPA administrator will take into account the cost of achieving effluent reduction, non-water quality environmental impact, and energy requirements (9).

After standards of performance are promulgated, it will be unlawful for any owner or operator of any new effluent or emission source to operate the new source in violation of any standard of performance applicable to such source (10). Regulations are now in existence for more than 40 different industries. Oil shale, of course, is not specifically regulated at this time.

Standards for Toxic Pollutants.

The FWPCA also mandates that the EPA administrator must maintain a list of toxic pollutants (11). Each toxic pollutant listed is subject to effluent limitations resulting from the application of the best available technology economically achievable for the applicable category or class of point sources (12). Criteria for best available technology economically achievable shall include characteristics of pollutants (chemical, physical, and biological), amounts, and the degree of effluent reduction attainable through the application of the best control measures and practices achievable, including treatment techniques, process and procedure innovations, and operating methods.

Section 307.(7) of the FWPCA also states, "Prior to publishing any regulations (establishing best available technology economically achievable), the EPA should consult with appropriate advisory committees, states, independent experts, and federal departments and agencies." Emerging technologies such as in situ oil shale processing should be prepared to make informed input to EPA.

If discharges meet the criteria established for (a) receiving waters, (b) best available control technology economically achievable for the applicable industry or (c) toxic pollutants, the EPA or state regulatory agency to which the authority has been granted may issue a permit for the discharge of any pollutant. The permit is a National Pollution Discharge Elimination System (NPDES) permit (13).

A regulation exists at the present time for allowing discharge based upon the water quality of the receiving water. While performance standards are subject to research, existing field facilities must comply with regulations designed to protect the quality of the receiving body of water.

Each state was given the opportunity to adopt water quality standards for the water of its state. Wyoming defines its water to include both surface and subsurface waters. The EPA has approved Wyoming's surface water quality standards and allows Wyoming to enforce the National Pollution Discharge Elimination System's permit system. In addition to surface water quality standards, standrads for pollution of groundwaters are being proposed in Wyoming.

In Wyoming the law prohibits any person, except when authorized by a permit, to alter the physical, chemical, radiological, biological, or bacteriological properties of any waters (14). The Wyoming act also forbids construction of any facility capable of causing or contributing to pollution. While standards of performance do not exist for the oil shale industry, LETC research facilities must comply with regulations based upon water quality for receiving waters. Hence, extensive data must be obtained for compliance purposes.

Subsurface Waters

Regulation of subsurface water pollution is rapidly developing. Wyoming recently proposed water quality criteria for seven classes of water. Contamination of subsurface water will then fall under their permitting system. Wyoming intends to maintain the physical, chemical, radiological, biological, and bacteriological properties of its subsurface waters. Consequently, in situ industries must be able to prevent contamination or restore water to its original condition.

Regulations promulgated under the Safe Drinking Water Act (15) will require State underground injection control (UIC) programs to prevent underground injection which endangers drinking water sources (16). Critical to the in situ oil shale industry will be definitions of "underground drinking water sources" and "underground injection."

The Act defined underground injection as the subsurface placement of fluids by well injection (17). Proposed definitions (18) defined well injection as "subsurface emplacement through a bored, drilled, or driven well." The proposal also defined an underground drinking water source as "any underground source with a level of total dissolved solids of 10,000 mg/l or less" (19).

The "regulations may not interfere with or impede (a) the underground injection of brine or other fluids which are brought to the surface in connection with oil or natural gas production, or (b) any underground injection for the secondary or tertiary recovery of oil or natural gas, unless such requirements are essential to assure that underground sources of drinking water will not be endangered by such injection" (20).

aquifers which in fact will not be protected because they are oil producing, are severely contaminated or located in such a way that use as drinking water is impracticable" (21).

Subsurface water quality standards will be extremely important to in situ oil shale development. The selection of in situ processing sites so that they do not interfere with subsurface waters or the development of restoration methods for such waters to their original quality are important considerations for control technology.

EXAMPLE PROJECTS INTEGRAL TO COMPLIANCE AND CONTROL

The previous discussion points out that there are federal and state regulations on water quality standards for both surface- and subsurface-produced aqueous effluents to which a potential in situ oil shale processing industry must adhere. Also field experiments must comply with all applicable regulations and meet established criteria for water control. In the absence of rigorously defined techniques and systems to control and simultaneously utilize produced waters, field experiments must employ certain expediencies which are acceptable under the law. An example of this is the use of containment and evaporation ponds constructed in accordance with state regulations and guidelines. While limited at this time in terms of employing sophisticated control technology capabilities at field sites, such sites do nevertheless offer prime opportunities for developing and demonstrating such capabilities. Despite of current limitations in applied control technology, field experiments can be conducted so as to meet applicable compliance criteria. The use of an evaporation pond serves to illustrate this point.

An evaporation pond will be used for disposal of process waters during operations at Rock Springs Site 12 (scheduled for operation in November 1978). This pond was designed to contain 100,000 gallons of water, was constructed in accordance with Wyoming Division of Environmental Quality (DEQ) guidelines for wastewater ponds, and required a permit from that agency. With respect to monitoring, the state requires that a leak detection system be incorporated as a design feature of the pond. However, research activities which will be associated with this pond also will include monitoring and analysis of volatile emissions, measuring evaporation characteristics, analysis of surface layer materials, analysis of dissolved solutes and changes resulting from weathering and biological activity determination of the amount and content of residues, and monitoring solar radiation, wind speed, wind direction, and ambient temperature. In addition, studies of pond liner compatability with process waters and shale oil were performed prior to the selection of the liner used in the pond. These studies exceed those required by the state, but utilize the opportunity afforded by the pond to better define pond characteristics. The additional data to be obtained from the Rock Springs Site 12 evaporation pond will provide the first characterization of physical and chemical aspects associated with ponding of process waters. These data

contingency measure or becomes integral to a treatment process (such as serving as a sedimentation step), these additional data will augment our knowledge of control procedures and options.

Discussion of the environmental research related to acquiring an in situ mining permit from the Wyoming DEQ for operation of Rock Springs Site 12 will serve as another example of projects integral to both compliance with regulations and development of water control technology. The in situ mining permit requires evidence of specific plans to restore any disturbed aquifer so that the water quality is equal to or better than it was prior to the activity. Figure 2 illustrates that, with respect to subsurface process waters, the ultimate objective is to demonstrate appropriate control so that no adverse environmental impact will occur. Three control approaches for achieving this are shown in the figure -- site selection, aquifer restoration, and process containment. The current plan leading to aquifer restoration will be discussed after a few remarks pertaining to the other two approaches.

The first approach is related to site selection criteria. The development of site selection criteria means that one must determine what type and to what degree subsurface environmental data are required in order to locate an in situ process where no groundwater impacts will occur even if ancillary subsurface control features are not used. It is possible that appropriate site selection would not require additional control of subsurface process waters if it could be established that there would be no contact between these waters and native groundwaters. Detailed hydrologic and geologic data may be required to determine such a finding. Specifically what data is required to allow for such site selection (including compliance data) is the focus of this approach.

The second approach, development of containment options, entails defining ways of lessening any intermingling of subsurface process waters with resident groundwaters. Diversion of aquifers up-dip of retort zones might be one option to be considered in this approach.

In the third approach, aquifer restoration, the present plan involves three interacting areas of activity. These are: site monitoring; solute leaching, transport, and interaction research; and field restoration trials. Each of these three activities will be discussed in turn. Site monitoring activities pertain to pre-operational, operational, and post-operational monitoring and analysis of subsurface waters located within, peripheral to, and at some distance from fracturing and in situ retorting experiments. Significant examples of this activity can be found in conjunction with Rock Springs Sites 4, 6, 9, and the current Site 12 operation (1). Post-operational monitoring of Site 4 has been in progress since this site was retorted in 1969. Monitoring of backflood waters, a subject significant to the leaching of spent retorts, is a part of each of these site activities. The water monitoring program being conducted in conjunction with Site 12 was developed using knowledge gained in prior experiments and will serve as a focal point for overall assessment of subsurface migration phenomena resulting from in situ experiments conducted in the Rock Springs area. In order to facilitate this task, all relevant water quality data are assembled in a computer system

At the same time, several studies are in progress dealing with the physical and chemical interactions associated with subsurface-produced water release and migration. Such studies include examinations of the leaching of retorted shale, the interaction of process waters with consolidated subsurface soils, sediments, and aquifer materials, and solute transformations in waters remaining or migrating from the retort zone. These studies are primarily oriented towards defining the mechanisms underlying phenomena observed during monitoring. This knowledge also will aid in the extrapolation of trends witnessed during monitoring activities to predict the ultimate probable fate and disposition of subsurface waters associated with in situ processing.

The third activity essential to the aquifer restoration plan involves field trials at the Rock Springs area. The previously described activities will serve to quantify and model aquifer disturbances. This field activity will explore and test methods for correcting any such disturbances. A preliminary step is the evaluation and selection of procedures. Two options are currently under consideration. One is to seal the retorted zone to prevent future contact between groundwaters and spent shale, and thus eliminate possible contamination through leaching. A project has been initiated in this regard which will select and test possible sealing agents (grout, cement, polymers, etc.) (22). One limitation of this option is that it does not address the question of process waters which may have been released during the course of retorting. Another option is to recover the process/groundwater eminating from the retort area and to treat such water at the surface to a degree suitable for reinjection into the retort zone. There is currently some evidence to suggest that a few cycles of this type would be sufficient to remove leachable materials from the retorted shale surface (22). This option would appear to be economically more attractive than the first option, especially since it uses treatment facilities which will be in place to treat surface-produced waters and because it may be relatively easy to equal or improve the quality of groundwaters (particularly at Rock Springs) through a treatment scheme.

As soon as sufficient data are available to decide which of the two options discussed is the more attractive, current plans call for testing the techniques at selected field sites. Use of the Rock Springs sites will take maximum advantage of the extensive site-specific data previously gathered during earlier activities (e.g., monitoring, transport and interaction research, and backflood water analysis). The efficacy of the option being tested could be determined largely through the use of existing monitoring wells. Following evaluation of the first field trial, a second, and more exacting, control experiment is planned. The second experiment is to be executed during 1981 at Site 12. An accelerated effort will be needed to achieve these field experiments. The goal is to demonstrate the selected aquifer restoration technique at Site 12 which will serve to advance our capabilities of subsurface process water control and will also serve to fulfill DEQ requirements for Site 12 as stipulated in the in situ mining permit. Such capabilities will then be available for application to other sites.

water control technology will be drawn from the several steps portrayed in Figure 2 related to biological effects research. Biological subjects being studied at LETC encompass terrestrial (plants and microorganisms), aquatic, and animal systems (1). The animal studies are primarily concerned with examining the health risks of occupational exposure to process waters that may be accidentally encountered at field sites or in the laboratory. The terrestrial, aquatic, and animal studies were initiated to fulfill two needs. The first need was to determine the impacts, if any, of process waters associated with LETC in situ processing field experiments on the local ecosystems and their components. This need was raised in the Environmental Assessment prepared for LETC field projects (24) in accordance with regulations established under the National Environmental Policy Act (NEPA). Biological impacts likely to occur as a result of failure of a containment or evaporation pond typifies the kinds of concerns raised in the Environmental Assessment.

The second need was to obtain information that would assist in the development of control technology for process waters. The control of process waters, particularly those produced at the surface, is primarily based on the development of treatment systems capable of upgrading the quality of the waters to a level satisfactory for their intended end use. It is therefore necessary to determine possible end uses of water along with the development of treatment systems. As previously mentioned, excess waters produced during in situ processing should be considered as a commodity. A potentially valuable use of excess waters would be for land applications, such as for agricultural irrigation or for revegetation of disturbed sites. If this application is to be pursued, then it is necessary to determine the level of treatment required in order to produce a water acceptable for land application. Characterization of constituents in treated and untreated waters and evaluation of legal restrictions on the quality of waters intended for surface disposal are two activities which help to determine required treatment levels. Screening the response of potential target organisms to process waters at various stages of treatment is a third activity being conducted at LETC to assist in the definition of treatment requirements. Through such biological screening studies, it is possible to determine what solutes or fractions in process waters are primarily responsible for adverse effects. Once this is determined, the capability of treatment methods to remove these materials can be considered. The final evaluation of the efficacy of the selected treatment procedure can also be tested through biological screening studies. In this manner, the biological screening work at LETC assists in determining treatment requirements and in assessing treatment procedures for waters potentially to be disposed of in land applications. Biological studies pursued for this purpose are deemed to be as integral to the overall development of control technology as the analytical characterization studies.

SUMMARY AND CONCLUSIONS

There are federal and state regulations on surface and subsurface water pollution. Emerging in situ fossil fuel technologies must be cognizant of these and develop process water control measures to insure compliance.

and demonstrating process water control. [illegible] in the emerging
industry. This paper has illustrated the approach in effect at the Laramie
Energy Technology Center to use in house field activities for advancement of
process water control technology while insuring compliance with regulations.

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5. Id. at Sec. 101 (a) (2).

6. Id. at Sec. 101 (a) (3).

7. Id. at Sec. 302.

8. Id. at Sec. 306.

9. Id. at Sec. 306 (b) (1) (B).

10. Id. at Sec. 306 (e).

11. Id. at Sec. 306 (a) (1).

12. Id. at Sec. 307 (a) (2).

13. Id. at Sec. 402.

14. Wyo. Stat. Sec. 35-11-301, (1977).

15. Safe Drinking Water Act of December 16, 1974, 42 U.S.Code 300f.

16. Id. at Sec. 1421 (b) (1).

Fed. Reg. 36737 (1976).

19. Id. at Sec. 146.2 (g)

20. 42 U.S.Code 300h.

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INTRODUCTION

Wastewater can be generated by several different sources within a shale oil recovery facility. The volume and quality of the wastewater from a particular source is dependent on the location and characteristics of the oil shale processed and on the type and size of recovery system used. The pollution potential may be high as in the case of retort water, or low as in the case of irrigation quality groundwater pumped from a mining area. Inclusion of an upgrading facility at a shale oil recovery complex will also impact the volume and quality of wastewater generated. Above-ground retorting facilities may reuse all of the wastewater streams available for moisturizing spent shale, although this is not necessary for all processes. Since moisturizing of subsurface spent shale is not required for in situ operations, wastewater may be discharged at these sites. However, modified in situ operations could use wastewater for moisturizing spent shale if shale mined from the in situ zones is retorted at the surface. In situ operations generate retort water in approximately the same volume as that of the crude oil produced. Therefore, a 50,000 barrel per day in situ facility would generate about 2 million gallons (16,000 m^3) of retort water per day. By comparison, an above-ground retort may generate only 200,000 gallons (1,600 m^3) of retort water per day at the same level of oil production.

This paper addresses studies undertaken at Pacific Northwest Laboratory to assess current technology for the treatment and disposal of shale oil wastewaters to maintain acceptable water quality levels in the receiving waters of the oil shale regions presently under development. Although the shale oil industry is largely in the pilot plant/demonstration phase, the codevelopment of adequate wastewater control technology is necessary for several reasons: 1) prevent environmental damage as a result of the pilot plant/demonstration operations themselves; 2) control techniques may produce water which can be reused in the production process and this should be taken into account in the design of full-scale facilities; 3) adequacy of control technology should be fully assessed at an early stage to obviate delays and problems in construction and/or operation of full-scale production facilities; and 4) characterization of effluent discharges from pilot plant/demonstration operations will facilitate other environmental and health assessments. The major oil shale deposits in the United States are located in Colorado, Wyoming, and Utah. Therefore, developers of the shale oil industry must be fully cognizant of the importance of conservation of the limited water supplies in this area.

LAND DISPOSAL

Land disposal of wastewater utilizes interactions between plants and the soil surface and matrix to achieve pollutant removal as the wastewater flows to the receiving water. Passage of the Federal Water Pollution Control Act PL 92-500 has focused attention on land disposal of wastewater as an alternative to be considered for complying with zero discharge requirements slated for 1985. Land

TREATMENT ASPECTS

Pollutant Removal Mechanisms

Removal of wastewater constituents is accomplished by physical, chemical, and biological processes with numerous and complex interactions occurring between these processes. The physical process of filtration provides the removal mechanism for suspended particulate matter in the wastewater. Soil and root microorganisms are responsible for biological degradation of numerous wastewater constituents. Both organic and in-organic compounds are broken down and/or utilized for metabolism by these microorganisms. Chemical processes, such as precipitation, ion exchange, oxidation and reduction, may occur to remove many inorganic and some organic substances. Precipitation of heavy metals, for example, is primarily responsible for removal of these constituents in soil, although ion exchange may be a contributing factor.

Land Application Methods

Existing land treatment facilities can be classified according to two different basic design patterns based on differences in liquid loading rates, land area requirements, and the interaction of the wastewater with vegetation and soil. The first method, infiltration, uses soil as purification medium while the second, overland flow, uses the land surface as the purification medium. Infiltration is further divided into two categories, irrigation and infiltration-percolation, which typically involve low and high rates of application, respectively.

Irrigation is the most common method of wastewater application. This is generally accomplished by sprinkler or spray methods. In areas where irrigation water is scarce, the system is managed to provide the maximum return from a crop, whereas in areas of sufficient water supply, criteria allowing maximum hydraulic loading are followed. Revenue realized from a crop is used to defray operating costs so deciding whether the system is to produce crops or treat effluent is important. Controlling soil salts is vital for plant growth to prevent buildup of toxic concentrations. This is accomplished by managing the wastewater salt concentrations and the rates of application.

Care must be taken to avoid overloading the system which prevents further infiltration of the applied wastewater. The soil can become clogged and the formation of shallow ponds can occur resulting in anaerobic conditions. Anaerobic bacteria can create slimes of incompletely degraded organic matter and particulates which are effective soil surface sealants. Other factors that can cause clogging are: 1) compaction from heavy weight; 2) the movement of fine grains of soil down from the upper zones; and 3) the formation of insoluble compounds from reactions between wastewater constituents and soil water and/or minerals.

wastewater composition is one of the most important factors to be considered when investigating the applicability of land treatment and disposal for a particular wastewater. The general criteria for judging the suitability of a wastewater for land disposal are given below:

1. The organic material must be biologically degradable at reasonable rates.

2. It must not contain materials in concentrations toxic to soil microorganisms. Since some toxic materials may accumulate through adsorption or ion exchange and approach toxic levels after prolonged operation, there must be reasonable assurance that this effect can either be prevented or mitigated.

3. It must not contain substances that will adversely affect the quality of the underlying groundwater. In many instances, decisions relative to this aspect of land disposal systems are difficult because of the uncertain nature of available estimating techniques.

4. It must not contain substances that cause deleterious changes to the soil structure, especially its infiltration, percolation, and aeration characteristics. An imbalance of sodium ion is a common problem in this regard.

Characteristics relevant to land disposal are presented for a number of different retort waters in Table 1.[1] All of the retort waters, except that from the Utah in situ test site, are from simulated in situ retorts at the Laramie Energy Research Center and the Lawrence Livermore Laboratory.

High salinity commonly found in the retort water would be toxic to most cover crops. Waters having conductivities greater than 2,250 μmhos/cm are considered unsuitable for irrigation in most cases. With the possible exception of one sample for which insufficient data are available (University of Southern California No. 1) none of the retort waters in Table 1 would be below 2,250 μmhos/cm conductivity following ammonia removal by stripping. Steam stripping tests would be required to establish accurate conductivity values for the ammonia stripped water.

Substances which could affect groundwater quality at a land disposal site receiving retort water are listed below:

- high salinity;
- high nitrogen concentrations which yield nitrate on oxidation; and
- refractory organics which are not oxidized or removed by the soil.

The high salinity found in most retort waters would adversely affect drinking water quality groundwater if sufficient dilution were not available in the aquifer. A limit of 500 mg/l is recommended for drinking water and this value is exceeded by more than 100% for all the retort waters listed in Table 1, even after steam stripping for ammonia removal. Furthermore, evaporation of water during irrigation and leaching of salts from the soil will add to the dissolved solids content of the retort water as it percolates to the groundwater.

TABLE 1. Retort Water Quality Data Pertinent to Land Disposal

Constituents	10 Ton Simulated In Situ Retort Runs, LERC[2]						
	S-29	S-31	S-32	S-33	S-35	S-36	S-37
Na^+, mg/l	210	1,300	1,200	160	530	960	150
K^+, mg/l	8	70	47	70	23	23	21
Mg^{+2}, mg/l	3.2	280	140	17	130	350	210
Ca^{+2}, mg/l	0.6	9.8	4.9	4.9	27	29	35
NH_3-N [includes NH_4^+], mg/l	14,200	10,500	13,500	8,900	5,100	4,800	--
Total Alkalinity, mg/l $CaCO_3$	40,800	34,000	47,000	20,500	17,200	13,900	8,200
Added Ca^{+2},(a) mg/l	3,900	1,420	440	4,460	400	1,300	--
Cl^-, mg/l	5,000	4,200	3,200	7,900	2,300	4,600	1,100
SO_4^{-2}, mg/l	1,600	1,600	320	2,100	380	1,800	1,400
Total Na^+, K^+, Mg^{+2}, Ca^{+2}, Cl^-, SO_4^{-2}, mg/l	10,700	8,880	5,350	14,700	3,790	9,140	3,736(d)
Total Filterable Residue, 103°C, mg/l	--	--	--	--	--	--	--
Total Organic Carbon, mg/l	6,060	3,880	2,830	10,660	4,970	9,370	33,350
Biochemical Oxygen Demand, mg/l	--	--	--	--	--	--	--
Chemical Oxygen Demand, mg/l	--	--	--	--	--	--	--
Conductivity After NH_3 Stripping,(b) μmhos/cm	>2,250	>2,250	>2,250	>2,250	>2,250	>2,250	>2,250

	University of Southern California[3]		LERC 150 tonne	Lawrence Livermore(c)	Utah in situ
	No. 1	No. 2	Retort, LBL[4]	7 Ton Retort	Test Site(e)
Na^+, mg/l	312	--	655	164	3,500
K^+, mg/l	3.5	--	37	28	90
Mg^{+2}, mg/l	48.4	16.4	24	2.3	16
Ca^{+2}, mg/l	14.9	4.6	3.3	1.5	<1
NH_3-N (includes NH_4^+), mg/l	4,790	--	8,360	25,000	3,060
Total Alkalinity, mg/l $CaCO_3$	--	--	38,000	80,500	14,500
Added Ca^{+2},(a) mg/l	--	--	--	--	0
Cl^-, mg/l	--	1,560	57	--	--
SO_4^{-2}, mg/l	59	930	1,100	--	--
Total Na^+, K^+, Mg^{+2}, Ca^{+2}, Cl^-, SO_4^{-2}, mg/l	--	--	1,900	--	--
Total Filterable Residue, 103°C, mg/l	--	--	4,210	--	13,500
Total Organic Carbon, mg/l	3,182	19,000	4,980	--	--
Biochemical Oxygen Demand, mg/l	5,500	350	5,330	3,000	3,400
Chemical Oxygen Demand, mg/l	20,000	12,500	8,800	8,660	8,200
Conductivity After NH_3 Stripping,(b) μmhos/cm	--	--	>2,250	3,800(d)	>2,250

(a) Ca^{+2} added as $Ca(OH)_2$ for ammonia stripping; Ca^{+2} mg/l = (mg/l NH_3 - N/14 mg/meq - mg/l Total Alkalinity/50 mg/meq) (20 mg/meq)
(b) Conductivity assumed to exceed 2,250 μmhos/cm when total ions exceed 1,200 mg/l.
(c) Analysis by Pacific Northwest Laboratory.
(d) NaOH added for stripping ammonia; conductivity measured on steam stripped water adjusted to pH 7.

concentration of ammonia, but other forms of nitrogen (nitrate and organic -N) may dictate the land requirement to attain the desired nitrogen loading. The nitrate and organic -N content of retort water has not been determined on a sufficient number of samples to establish an average or range of values.

Steam stripping of ammonia is more effectively accomplished at high pH levels. Stripping efficiency is reduced as neutrality is approached and becomes low for acidic solutions. Additional alkalinity in the form of lime is frequently added to maintain adequate pH levels. The addition of lime in the stripping process substitutes Ca^{+2} ion for ammonia ion which is beneficial from the standpoint of the ratio of Na^+ to Ca^{+2} plus Mg^{+2}. However, if considerable lime is required, the salinity of the steam stripped waste will be high due to the calcium salts present. The alkalinity deficit reported as added Ca^{+2} (lime) for steam stripping is given for most of the retort waters in Table 1. Removal of all the ammonia may not be required since some nitrogen will be required for vegetation growth and oxidation of the organic matter in the retort water. In addition to ammonia, nitrogen can be supplied by organic-nitrogen and nitrate-nitrogen in the retort water.

The generally high ammonia levels in retort water would be expected to cause toxicity problems if not removed prior to disposal of the water to land. Although removal of the ammonia may be relatively costly, part or all of this cost may be recovered by marketing the ammonia. It is likely that steam stripping would be used to remove the ammonia since this process is well adapted to removal of high concentrations of ammonia from wastewater. Steam stripping is the standard industrial process used for removal of ammonia from coking liquors and petroleum refinery sour water. Sufficient alkalinity must be available in the retort water to allow conversion of NH_4^+ ion to volatile NH_3 which is stripped by the steam passing counter-currently to the water in the stripping column. Alkalinity and ammonia data on only one retort water, Utah in situ test site, indicate sufficient alkalinity to steam strip the ammonia. Addition of alkalinity would probably be required for the other retort waters. The total alkalinity reported for these waters cannot be considered an accurate guide, however since the end point pH for alkalinity titration may be well below pH 7. Ammonia stripping efficiency has not been adequately defined to date for assessing this aspect of land disposal. Furthermore, a pilot study may be required to accurately establish the optimal nitrogen loading.

It is possible that some of the organic constituents in retort water will be resistant to oxidation and might eventually be leached into the groundwater causing some deterioration in the quality of the groundwater. A low BOD relative to a COD could indicate a large fraction of the organic matter in the retort water is not readily biodegradable. Therefore, it is anticipated that low loading rates will be required to allow sufficient time for oxidation of the organics by the biota in the soil. The generally high organic content would appear to be the limiting factor on application rates of retort water to land rather than hydraulic characteristics. Furthermore, refractory organics which would not degrade even under low loading rates would leach through to groundwater.

or retort water. No data are available on the presence of organic substances which may cause problems.

Substances which cause plugging of the soil commonly include sodium ion (when it is unbalanced with Ca^{+2} and Mg^{+2}) and suspended solids (nonbiodegradable). Suspended solids can plug the pores of the soil through the process of filtration, while sodium ion can cause dispersal of the clay particles in the soil thus sealing the pore structure. Currently, data are insufficient to evaluate the possible effect of suspended solids in retort water on land disposal, but at least part of the suspended matter in retort water is expected to be removed in the pretreatment steps for ammonia stripping to avoid fouling the stripping column. Air pollution from volatile organic constituents in this waste is also a potential problem. Retort water generally has an offensive odor which would not be well received by downwind recipients from the disposal site. Consideration would also have to be given to the possible presence of volatile toxic organics or other organics which would degrade air quality in the region.

Effect of Climate

The long winters characteristic of the oil shale regions of Colorado, Utah, and Wyoming adversely affect the cost of land disposal by irrigation and overland runoff due to the large wastewater storage requirement. Irrigation and overland runoff are not possible during extended periods of freezing temperatures and application rates must be reduced during cool weather. Based on the length of frost free seasons, storage requirements range from 5 to 10 months, however, specific site operations may decrease the storage area needed.

UNDERGROUND INJECTION

Underground or deep well injection is a disposal method which seeks to isolate a liquid waste in a geologic strata to eliminate, as nearly as possible, any environmental impacts resulting from disposal of the waste. Geologic strata selected to receive wastes by this method are generally located at a considerable distance from ground surface to provide additional assurance of confinement and avoid contaminating freshwater aquifers near the surface. Underground injection is normally reserved for wastewaters which are very difficult or expensive to treat for release to surface receiving waters. It is used extensively for the disposal of oil well brine wastes.

UNDERGROUND INJECTION WELLS

A typical well consists of several pipes extending below the surface. The function of each of these pipes is as follows:

Conductor Pipe - This is the first of several concentric pipes that are placed into a disposal well. It extends between 30 and 60 m below the surface and prevents shallow water contamination while the surface hole is being drilled. This pipe is usually driven into place with a pile driver.

Surface Casing - This pipe extends from the surface to approximately 60 m below the base of the freshwater. This casing is cemented in place back to the ground

below the disposal zone, depending upon the type of completion intended. This casing is also cemented back to the surface and inside the surface casing. Its purpose is to seal off the formation above the disposal zone and below the freshwater.

Injection Tubing - This pipe is the conduit through which the effluent travels to the disposal zone. It is always sealed at the well head and usually just above the disposal zone. The annular space between the protecting casing and injection tubing is filled with a noncorrosive fluid. Pressure should be applied to this annulus approximately 35,000 kg/m² higher than the injection pressure. The higher annular pressure will prevent any flow of effluent into the casing tubing annulus.

Disposal Zone Completion

If the well is completed in a sand formation, the gravel packed sand screen completion method should be used. If the well is completed in a limestone formation, open hole or perforated completions are acceptable.

WASTE CHARACTERISTICS

The suitability of waste for underground injection depends on its volume and physical and chemical characteristics, and on the physical and chemical properties of the potential injection zones and their interstitial fluids. Wastewater that is desirable for injection must be: 1) low in volume and high in pollutant concentration; 2) difficult to treat by surface methods; 3) free of any adverse reaction with the formation fluid or the strata; 4) free of suspended solids; 5) biologically inactive; and 6) noncorrosive.

Waste disposal into underground aquifers constitutes the use of limited storage space, and only concentrated, very objectionable, relatively untreatable wastes should be considered for injection. The fluids injected into deep aquifers do not occupy empty pores, but displace the fluids which saturate the storage zone. Consequently, optimal use of the underground storage space will be realized by the use of underground injection only when more satisfactory alternative methods of waste treatment and disposal are not available.

Reaction of the wastewater with the formation water or the strata is important. Resulting problems could include dissolving the formation, generating a gas or precipitate in the formation, and clogging by biological growths. The wastewater should be free of suspended solids and biologically inactive to avoid reservoir clogging. The corrosiveness of the wastewater should be low to prevent tubing and pump corrosion.

Retort water characteristics vary depending on the type of oil shale, retorting process, and retort operating conditions. As shown in Table 1, BOD_5 values range from 350 to 5500 mg/l and filterable residue from 150 to 101,000 mg/l. Ultrafiltration may be necessary to remove the suspended solids. Biocide addition may be necessary because high BOD concentrations promote biological activity.

ammonia concentrations in the retort water should prevent biological activity. When ammonia concentration is reduced, (either by treatment for ammonia recovery or by ion exchange during migration of fluid in the disposal zone) the probability of biological activity is increased. If necessary nutrients (mainly Ca, Mg, and P) are present in the disposal zone, biological activity of the retort water is almost certain. Plugging of the injection zone by bacterial growth and by gas formation (CH_4 and CO_2) is likely to occur unless very long residence times in the injection zone are permitted for further reaction.

DISPOSAL SITE SELECTION

Great care must be exercised in the selection of an underground disposal site for liquid wastes. The suitability of a specific location of a waste injection well must be evaluated by a detailed geological subsurface investigation. However, regional geological conditions can be used to evaluate general suitability of certain areas.

Certain areas of the continental United States, such as the Rocky Mountains, are generally unsuitable for waste injection wells because igneous or metamorphic rocks lie at or near the ground surface. Such rocks do not have sufficiently high porosity or permeability to warrant their use as a disposal formation. Areas with extensive extrusive volcanic sequences exposed are also not suitable for waste disposal wells. Even though these rocks have porous zones, they usually contain freshwater.

The final appraisal of a disposal well site is usually determined by a two-phase geologic investigation. The first phase includes an evaluation of potential sites on the basis of available data. The second phase consists of a more detailed evaluation of subsurface conditions based on information obtained from drilling a pilot hole or the injection well.

Information sought during the first phase of the investigation and prior to the installation of an injection well includes the extent, thickness, depth, porosity, permeability, temperature, water quality, and piezometric pressure of potential injection zones. The presence of impermeable confining beds, lateral changes in rock properties, the existence of faults or joints, and the occurrence of any mineral resource in the area must also be evaluated. Existing wells in the area which may penetrate the potential injection zones must be located because liquid wastes could escape through these wells if not properly plugged.

The second phase of the investigation is conducted during the drilling and testing of the injection well. Often the actual injection zone is not selected until the well has been drilled and a number of potential zones have been tested and until the chemical quality of water in the potential zones has been evaluated. Pumping tests are used to measure the permeability and water samples are obtained for chemical analysis. Other important rock properties are measured by geophysical logging, drill-stem testing tools, or by laboratory tests on core samples. The results of these geologic investigations are used not only in evaluating the feasibility of subsurface waste disposal, but also to provide basic data for designing the injection well and the optimal rate of injection.

federal, state, and local agencies and industries to develop comprehensive programs to prevent or eliminate groundwater contamination and to improve sanitary conditions of these waters. In 1974, EPA issued "Administrator's Decision Statement No. 5" as agency policy on injection wells and subsurface emplacement of fluids by well injection. This policy was drafted to protect the subsurface from pollution or environmental hazards as a result of improper injection practices and poorly sited injection wells. Under this policy, EPA opposes the emplacement of wastes by injection without strict controls and a clear demonstration that such emplacement will not interfere with present or potential use of the subsurface environment, contaminate groundwater resources, or otherwise damage the environment. EPA can require that all proposals for subsurface injection be critically evaluated to determine that the following guidelines have been met:

- All reasonable alternative measures have been explored and found less satisfactory in terms of environmental protection.

- Adequate preinjection tests have been made for predicting the fate of materials injected.

- There is conclusive technical evidence to demonstrate that such injection will not interfere with present or potential use of water resources nor result in other environmental hazards.

- The injection system has been designed and constructed to provide maximal environmental protection.

- Provisions have been made for monitoring both the injection operation and the resulting effects on the environment.

- Contingency plans that will prevent any environmental degradation have been prepared to cope with all well shut-ins or well failures.

- Provisions will be made for plugging injection wells when abandoned and for monitoring plugs to ensure their adequacy in providing continuous environmental protection. Also under this policy, EPA acknowledges that subsurface injection of wastes is only a temporary means of disposal until new technology that will ensure a higher degree of environmental protection becomes available.

In December of 1974, the National Safe Drinking Water Act was passed by Congress. The purpose of this legislation was to ensure that water supply systems meet minimum national standards for the protection of public health. The Act was designed to achieve uniform safety and quality of drinking water in the nation by identifying contaminants and establishing maximum levels of acceptability. The major provision of the Act that encompasses the underground injection program is the establishment of regulations to protect the underground drinking water sources by the control of subsurface injection.

Various states are to have enforcement responsibility for groundwater protection. If a state underground injection control program is to be approved by EPA, it must:

- prohibit injection after December 17, 1978, unless by permit;

- allow permits for underground injection only when the applicant can prove that injection will not endanger drinking water sources;

- provide for inspection, monitoring, record keeping, and reporting to EPA; and

- include no requirements that interfere with underground water or brine injection in oil or gas production, or for secondary or tertiary oil recovery, so long as freshwater aquifers are unaffected.

If a state does not have an approved underground injection control program, EPA should assume enforcement responsibilities.

In August 1976, EPA issued the proposed new 40 CFR Part 146 setting forth the regulations governing stage underground injection control (UIC) programs. The intent of this proposed regulation is to:

- establish minimum requirements for effective state programs to protect existing potential underground sources of drinking water from being endangered by the underground injection of fluids;

- provide improved protection of public health by controlling certain potential sources of underground drinking water contamination;

- provide minimal national control;

- allow a state to exercise maximum flexibility to develop programs to meet their needs, noting that differences exist between states, including geological conditions, use and availability of groundwater, and intensity of underground injection operations; and

- provide a program that would not be excessively costly to the states or to most injectors.

TREATMENT OF RETORT WATER

Bench-scale treatability studies are being conducted to evaluate current technology for the removal of pollutants from shale oil wastewaters. Retort waters generated by pilot plant and in situ test facilities are used in these studies to assess the adequacy of treatment processes to achieve the desired effluent quality. The wastewater treatment process selected for evaluation are essentially patterned after technology used by petroleum refineries.

EVALUATION CRITERIA

In the absence of sufficient waste treatment data to develop guidelines for disposal of retort or process wastewater to surface receiving waters, tentative evaluation criteria based on state standards are provided in Table 2. Except for total dissolved solids, these values are taken from water quality standards

No.	Parameter	Limitation
1	BOD$_5$	30 mg/l
2	Suspended Solids	30 mg/l
3	Oil and Grease	10 mg/l and no Visible Sheen
4	pH	6.0-9.0
5	Settleable Solids	Essentially Free From
6	Floating Solids	Essentially Free From
7	Taste, Odor, Color	Essentially Free From
8	Toxic Materials	Essentially Free From
9	Total Dissolved Solids	500 mg/l

Note: Numbers 1-4 above provide specific limitations for discharge of wastes not covered by other industrial effluent limitation guidelines in the State of Colorado. Numbers 5-8 are standards applicable to receiving waters for Colorado, Utah, and Wyoming. Number 9 is the average total dissolved solids in the Colorado River at Grand Valley, Colorado.

and effluent limitations for the states most likely to be involved in shale oil development (Colorado, Utah, and Wyoming). The limitation of 500 mg/l for total dissolved solids represents an average value for the Colorado River at Grand Valley, Colorado, which is in the vicinity of several planned commercial shale oil recovery operations. Discharges of effluents containing more than 500 mg/l TDS into the Colorado River in this area could ultimately increase the salinity above control limits for this river as it crosses the border into Mexico. Total suspended solids for retort waters listed in Table 1 exceed 500 mg/l with but one possible exception (USC No. 1) after ammonia removal. Discharge of retort water to surface receiving waters is, therefore, unlikely without desalination.

Four out of five BOD values listed in Table 1 are two orders of magnitude or greater than the effluent limitation of 30 mg/l given in Table 2. It is unlikely that a practical biological treatment scheme could meet this limitation, however, subsequent chemical coagulation, sedimentation, filtration, and activated carbon sorption should achieve a very high level of removal. If this sequence of treatment processes cannot meet the limitations presented in Table 2, less stringent criteria may be applied. In some areas more stringent criteria may be necessary to protect local surface receiving waters.

Retort water can potentially contain several toxic materials. Ammonia, which is highly toxic to fish and other aquatic organisms, is present at relatively high concentrations. Most of the ammonia must be removed before biological treatment can be used to degrade organic material contained in this waste. Arsenic is also present at several mg/l in some retort waters and could interfere with biological treatment. Furthermore, removal would be required prior to discharge to surface waters. Other unidentified substances (e.g., organic substances) could also cause toxicity problems in biological treatment or in surface receiving waters.

BENCH-SCALE TREATABILITY STUDIES

Steam Stripping

Bench-scale studies were conducted to evaluate steam stripping as a means of removing ammonia from retort water. The steam stripper used in this work consisted of a two-inch ID glass pipe packed to a depth of four feet with 1/4-inch ceramic saddles. Feed to the stripper is introduced at the top of the column of saddles and is counter-currently contacted with steam generated by a reboiler at the bottom of the column. Steam, containing volatile constituents stripped from the feed, is removed from the top of the column, condensed, and collected in a condensate receiver. The condensate receiver is vented to a water trap and an acid trap in series to absorb ammonia vapor carried over with non-condensable gases. The steam stripped feed collects in the reboiler and is drawn off continuously to maintain the desired liquid level in the reboiler. Two operational modes were evaluated, one with recycle of the condensate and one without recycle. The condensate is recycled by injecting it into the feed stream to the stripping column. Recycle of the condensate eliminates the necessity of dealing with a separate wastewater stream but also reduces the efficiency of ammonia removal in the stripping column by increasing the ammonia concentration in the feed streams. The alternative of no condensate recycle results is an aqueous ammonia solution which contains volatile organic matter stripped from the retort water.

The steam stripping studies were performed using a sample of retort water from an in situ operation in Utah which contained 3100 mg/l ammonia. Ammonia removal with recycle of the condensate averaged 90% for 2 runs at a boiloff rate of 4.5%. Over 99% of the ammonia was removed without recycle of the condensate at a boiloff rate of 5.3%. Steam stripping also reduced the alkalinity from 14,300 mg/l to about 4,700 mg/l. However, the pH of the retort water increased from 8.8 to about 10 because of carbon dioxide stripping. Excessive foaming occurs in the reboiler which requires precise liquid level control to prevent the foam from entering the column where it causes flooding.

Some fouling of the packing in the stripping column was observed, which may have been the result of suspended matter depositing on the packing. Although settled retort water was used, it contained about 150 mg/l of suspended solids, which were reduced to about 30 mg/l through the stripper. A small volume of light oil was also removed by the steam stripping operation. Organic carbon removal by steam stripping ranges from 15 to 20%.

A sample of retort water from the Lawrence Livermore Laboratory (LLL) was steam stripped while operating in the condensate recycle mode at a condensate temperature of $85.5 \pm 3.5°C$. The ammonia was reduced by 99.5% from 26,500 mg/l to 135 mg/l at a boiloff rate of 15% of the combined feed and condensate recycle. This boiloff rate is equal to 18% of the feed flow alone. Approximately 1/4 of the ammonia was recycled with the condensate stream and 3/4 was evolved from the condensate receiver as a gas. The feed flow to the stripper column with the LLL retort water was restricted to about half that of in situ test site retort water to avoid flooding in the column. This is believed to result from a greater gas flow ($CO_2 + NH_3$) up the column with the LLL retort water.

One of the retort water samples came from the 6000 kg simulated in situ retort at the Lawrence Livermore Laboratory, one from an above-ground retort in Colorado, and the other three samples from an in situ test site in Utah. Both aerobic and anaerobic biological treatment processes have been evaluated on a bench-scale. Aerobic treatment consisted of activated sludge or combined roughing filter (trickling filter) and activated sludge. The results of the aerobic treatment studies indicated toxicity problems in the treatment units as the concentration of retort water was increased in the feed to the units. Good biological growth and organic carbon removals were observed during the initial phases of the acclimation period but an apparent toxicity problem develops as the percent actual retort water in the feed increases and the percent artificial retort water decreases. Analysis of the retort water for toxicants revealed the presence of arsenic and thiocyanate. Thiocyanate is not believed to be a problem since the concentration of this constituent is below the threshold value of 500 mg/l for activated sludge. Arsenic could be a problem since it exceeds the threshold value of 0.1 mg/l for activated sludge. The Livermore sample contained 1.3 mg/l arsenic and the remaining samples contained 4-13 mg/l arsenic. Results of anaerobic digestion studies conducted with 3.5 liter digesters also indicated toxicant problems. Gas production from the digesters diminished steadily as the concentration of actual retort water was increased.

Results of studies to evaluate powdered activated carbon addition to the anaerobic digesters indicate successful operation in the case of the Livermore retort water, but continued toxicity problems with the other retort water samples. The powdered activated carbon is effective for removing certain soluble organics, including toxic organics, from solution which could reduce the stress on microbial population in the digesters. The activated carbon is also effective in some instances for removing heavy metals from solution, but its effect on arsenic in retort water is unknown at the present time. Analysis for soluble arsenic in the digester receiving in situ test site retort water revealed 0.96 mg/l which is near the toxicity threshold for anaerobic digestion. Soluble arsenic in the digester receiving Livermore retort water was 0.56 mg/l. Preliminary results indicate that activated carbon treatment of Utah in situ retort water will permit aerobic biological degradation to take place although the amount of activated carbon needed may be relatively high.

MINEWATER TREATMENT

Water pumped from underground oil shale mines or in situ operational zones in an oil shale formation may contain pollutants, such as fluoride, boron, and high dissolved salt concentrations, which will prevent unrestricted release of this water to surface receiving streams. Treatment and disposal technology for these minewaters is also being assessed.

FLUORIDE REMOVAL STUDIES

Treatability studies were conducted to evaluate methods for removing fluoride and boron from minewater. The results of bench-scale experiments with groundwater taken from a site in Colorado show a 50% breakthrough capacity of 350 bed volumes for fluoride removal by activated alumina adsorption. The groundwater fluoride concentration was 20 mg/l; therefore, the fluoride capacity is approximately 7 g/l of activated alumina. In order to achieve effective fluoride

regenerated with dilute sodium hydroxide, it is necessary to add additional acid to the feed at the beginning of the exhaustion cycle to neutralize the residual caustic regenerant in the bed. The acid addition for pH adjustment of the feed is expected to represent a substantial portion of the chemical cost of treatment for fluoride removal by activated alumina adsorption. An estimated 13¢ per thousand gallons of groundwater would be required to adjust the pH with sulfuric acid priced at $50 per ton of acid. Regenerant costs are estimated to be 16¢ per thousand gallons of groundwater treated based on sodium hydroxide priced at $280 per ton.

Results of precipitation experiments with simulated groundwater indicate 90% fluoride removal with phosphoric acid and lime addition. Approximately 9 moles of phosphorus and 10 moles of calcium per mole of fluoride are required to achieve this level of fluoride removal which would be needed to allow discharge of the groundwater to nearby surface receiving waters. The precipitation formed is basically a mixture of fluorapatite, $Ca_5F(PO_4)$, and hydroxy apatite, $Ca_5(OH)(PO_4)_3$. The cost of phosphoric acid and lime to treat the groundwater is estimated to be about $2 per thousand gallons, which is excessive relative to other treatment methods.

Ion exchange with a weak base anion exchange resin was investigated as a unique process which showed some potential because of the low selectivity of this resin for bicarbonate, the principal ion competing with the fluoride. Laboratory results showed a correspondingly low selectivity for fluoride which negates possible advantages this process may have over other ion exchange processes.

BORON REMOVAL STUDIES

Boron removal from the groundwater is not effected by either activated alumina or lime and phosphate treatment. Bench-scale studies with a boron selective ion exchange resin indicate good boron removal from 2000 bed volumes of groundwater containing 0.6 mg/l. Boron removal to less than 0.3 mg/l is required for discharge to nearby surface waters.

SUMMARY AND CONCLUSIONS

Current data in the literature indicate that the salinity of retort water from shale oil recovery operations will be too high in most cases for irrigation of cover crops needed for effective stabilization by land treatment and disposal. Furthermore, large storage lagoons would be required to hold the retort water during the long winters encountered in the oil shale regions of Colorado, Wyoming, and Utah. Additional problems which may arise with land disposal include air pollution from volatile constituents and groundwater pollution from refractory organics and dissolved salts in the retort water.

Regulatory restraints are expected to limit the use of underground injection for disposal of highly polluted shale oil wastewaters. Proof of confinement of injected wastes will be required to assure protection of drinking water resources, and this is often difficult and costly to accomplish. Underground injection of wastewater is a viable disposal option, however, where all reasonable alternatives have been explored and found to be less satisfactory in terms of environmental protection.

carbon addition appears to overcome the toxicity problem in some instances.

Fluoride removal from minewater with activated alumina and fluorapatite precipitation was investigated. Reagent costs for the precipitation were estimated to be $2 per thousand gallons whereas reagent costs for activated alumina treatment were only 29¢ per thousand gallons. Boron was effectively removed by ion exchange on a boron specific resin.

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INTRODUCTION

In modified in situ (MIS) oil shale retorting, the resource is processed in the ground. Porosity is introduced into the formation by mining out from 20 to 30% of the in-place oil shale. This material is brought to the surface and either processed in surface retorts or stockpiled. The balance of the material is rubblized underground using various mining techniques. Oil is extracted by pyrolysis and combustion.

This process produces oil, a low BTU gas and process water and leaves behind large underground chambers (retorts) of spent shale and surface piles of raw or spent shale. The acceptability of MIS retorting may depend on the resolution of several environmental issues related to these residuals including groundwater disruption, resource recovery, retort stability and solid and liquid residual disposal.

The purpose of this paper is to investigate the feasibility of returning the solids stockpiled on the surface and process water to the abandoned underground chambers. We believe that potential environmental problems can be largely overcome by returning on-site waste materials to the abandoned underground retort. This would fill the void space created by mining, thus improving structural strength and reducing permeability to groundwater flow. If sufficient strength could be developed, it may be possible to design retorts so that the pillars could be retorted and resource recovery improved. It would also result in the simultaneous disposal of solid and liquid residuals.

CONTROL STRATEGY

Various materials could be introduced into an abandoned retort or surrounding strata to increase structural strength or to reduce the flow of groundwater through the retort. These materials, called grouts, have been widely used in a number of fields including oil field reservoir engineering, nuclear waste containment, gas storage in underground formations, deep coal mining, soil consolidation and various construction activities. The nature of these conventional materials needs to be explored to determine the types of grouts that may be produced from on-site waste materials and properties required for retort sealing.

(1) The grouted area must be impermeable enough to prevent the degradation of local ground water or surface water.

(2) The grouting material must be chemically stable in the presence of saline groundwater.

(3) The grout viscosity must be low enough and the setting time long enough for the slurry to penetrate a large area.

(4) The grouted area should be able to withstand both hydrostatic and overburden pressures. The hydrostatic pressure is due to natural head differences that exist between the aquifers surrounding the oil shale deposits in some areas and to significant dewatering during retorting.

An impressive array of commercially-available grouting materials has been used in other industries. These have been extensively described in the literature (1, 2) and include cement and chemical grouts. Cement grouts typically have long setting times, are non-Newtonian and have relatively high viscosities compared to chemical grouts. Chemical grouts are water solutions of various inorganic or organic compounds and are most typically based on sodium silicate, acrylamide, polyphenolic and urea-formaldehydes, lignins, and resins. Properties and cost factors for some of these grouts are compared with spent shale in Table 1. Preliminary estimates indicate that it could cost from 20 to 270 dollars per barrel of oil for the grouting material alone if abandoned retorts were sealed with these conventional materials. Spent shale grouts, on the other hand, may be economically feasible if technical problems associated with their use are resolved.

The high costs of conventional grouts and the on-site availability of some of the raw materials necessary to manufacture them, suggests that waste products be used to produce grouts. Readily available materials include raw and spent shale, latent heat within the retort, gases, process water and mine water. These materials should be considered as raw materials for on-site manufacture of grouts that would not be economically competitive if purchased from commercial sources. Many of these components show promise for use as grouting materials. Some possibilities include on-site conversion of raw or spent shale into a pozzolan or cement, use of NH_3 in the gas and process water to produce urea-formaldehyde polymers, use of CO_2 in the gas and Na_2CO_3 in the process water to produce insoluble carbonate deposits, and the manufacture of silica gels from mine water, retort waters or offgas.

There are many possible solutions to the retort abandonment problem using these on-site waste products. The most appropriate one will depend on desired strength increase, permeability reduction, retort/aquifer geometry and cost. The following sections of this paper will discuss the use of spent shale and process water as major components of a grout and methods of distributing the grout in the retort.

Table 1. Comparison between conventional grouting materials and spent shale

Class	Example	Viscosity before gelling, cp (range)	Gel time min. (range)	Cost factor relative to neat cement	Potential Application	
					Hydraulic barrier	Provide structural Strength — Medium
Cement	Portland cement slurry (neat)	(a)	10-300	1.0	x	x
Silicate	Water glass (sodium silicate)	1.5-2	0.1-60	1.3	x	x
	Injectrol G (3)					
Polymer	AM-9 polyacrilamde (1)	1.2-1.6	0.1-300	7.0	x	x
	PWG (3)	1.5	->300	9.0	x	x
Resins	Herculox (3)	13	4-60	4.5	x	x
	Epseal (3)	80-90				
Emulsions	Asphalt 65% (4)				x	
Foams	Polyurethane foam (5)		15	1.5	x	
Spent shale	Lurgi (6)	(a)	28 days	0.05		
Lignin base	Blox-All (2)	8-15	3-90	1.65	x	
Unsaturated fatty acid	Polythixon FRD (2)	10-80	25-360		x	
Elemental sulfur		7 cp @ 159 C	sets when cool	available at low cost from gas refining sites		
Formaldehyde base	Urea-formaldehyde (2)	3.5-13	1-60	6.0	x	

(a) Depends on the water-cement ratio (WCR) and presence of additives. With a WCR of 45%, and no additives, the viscosity of cement is 200 cp. Addition of a slurry fluidizer (i.e., naphthalene polymer) may reduce this to 20 cp. By comparison, of 450% to 900% is needed to reduce the viscosity of Lurgi spent shale to 200 cp.

strength-forming material (7). The chemical composition of spent shale is compared with pozzolans in Table 2. This comparison shows that spent shale appears to meet the chemical requirements for ASTM Class C pozzolan and is very similar to natural pozzolans. This is of considerable interest because the spent shale could be used to reduce permeability and provide strength development of an abandoned MIS retort.

Two studies have been conducted on the use of surface spent shale to manufacture a cement-like material. However, these have met with limited success (possibly due to low temperatures reached in the surface retorts). Culbertson, Nevens and Hollingshead (7) studied the stabilization of spent shale from a TOSCO retort. Shear strength and confined compressive strength in the range of 250 to 500 psi were obtained. Strength development was positively correlated with the amount of cohesive hydrates formed. After 15 days of setting, no loss of strength occured in samples resaturated with water.

Nevens, Habenicht and Culbertson (6) studied the filling of a simulated in-situ retort with a slurry of Lurgi spent shale. Samples calcined at 750 to 850 C required from 500 to 1000 wt % water to reduce the viscosity to 100 cp. Compressive strengths obtained after 28 days ranged from 5 to 200 psi.

Although results with 100% spent shale grouts have been discouraging to date, research is in its infancy and advances may occur. The most promising possibility is to use spent shale to create a hydraulic lime-pozzolan mortar. This is a mixture containing active lime (CaO) and pozzolanically active silica (SiO_2) and alumina (Al_2O_3) which yield cohesive hydrates when mixed with water. This strategy is explored here by contrasting the chemistry of cements, pozzolans and mineralogical changes that occur during oil shale retorting.

Cement, pozzolan and oil shale chemistry

The chemistry of pozzolan and cement and of the carbonate/silicate minerals in oil shale is germane to understanding the potential role of spent shale as a grout. Cements are prepared by blending proper proportions of finely ground limestone and clay and firing the mixture in a kiln at 1450 to 1550 C. The resulting clinker is cooled, about 5% to 6% gypsum is added as a set retarder and the mixture is pulverized. When water is added to this material and the paste is allowed to set it will gradually convert to a hardened product. This process can be represented by the following set of chemical equations:
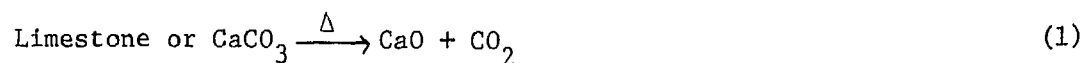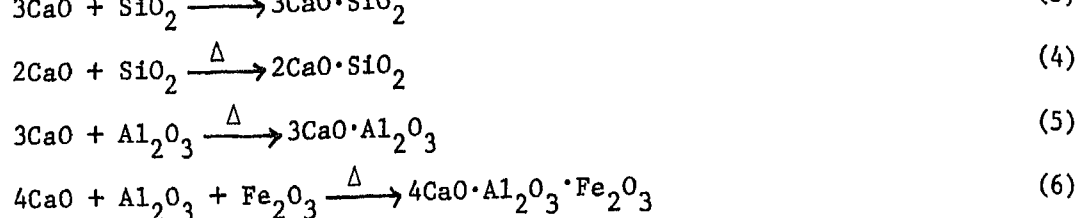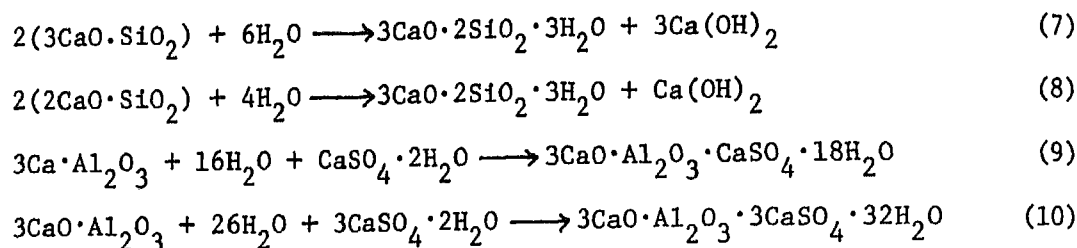
Calcining

$$\text{Limestone or } CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \tag{1}$$

$$\text{Clay} \xrightarrow{\Delta} Al_2O_3 + SiO_2 + Fe_2O_3 \tag{2}$$

Table 2. Composition of pozzolans and spent shale

Constituent	Oxide analysis, weight percent			
	typical natural pozzolan (9)	typical industrial pozzolan (lignite fly ash) (10)	combustion run spent shale	ASTM C-618-78 class C pozzolan (11)
SiO_2	55.0	28.7	46.5	⎫
Al_2O_3	17.7	12.0	10.7	⎬ >50.0
Fe_2O_3	3.5	6.8	4.2	⎭ −
CaO	3.2	40.5	17.2	−
MgO	1.0	7.4	7.8	−
SO_3	−	2.5	−	<5.0
FeO	0.9	−	−	−
K_2O	6.4	−	3.0	−
Na_2O	3.4	0.6	3.3	−
Loss on ignition	6.3	0.4	1.6	<6.0

$$3CaO + SiO_2 \longrightarrow 3CaO \cdot SiO_2$$

$$2CaO + SiO_2 \xrightarrow{\Delta} 2CaO \cdot SiO_2 \tag{4}$$

$$3CaO + Al_2O_3 \xrightarrow{\Delta} 3CaO \cdot Al_2O_3 \tag{5}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \xrightarrow{\Delta} 4CaO \cdot Al_2O_3 \cdot Fe_2O_3 \tag{6}$$

Hydration

$$2(3CaO \cdot SiO_2) + 6H_2O \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \tag{7}$$

$$2(2CaO \cdot SiO_2) + 4H_2O \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \tag{8}$$

$$3Ca \cdot Al_2O_3 + 16H_2O + CaSO_4 \cdot 2H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 18H_2O \tag{9}$$

$$3CaO \cdot Al_2O_3 + 26H_2O + 3CaSO_4 \cdot 2H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \tag{10}$$
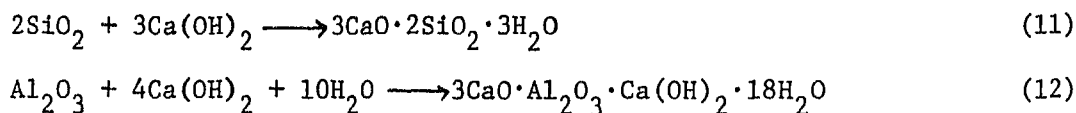
It would not be economically feasible to manufacture cement on site because of the high energy requirements (8). However, a hydraulic lime-pozzolan could be produced at temperatures much below clinkering temperatures.
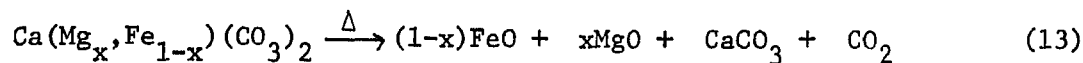
Pozzolans are siliceous and aluminous materials that react with lime in finely divided form and in the presence of moisture to form cohesive hydrates. These hydrates are the main strength-giving compounds of hydrated cement. Typical pozzolanic reactions are:

$$2SiO_2 + 3Ca(OH)_2 \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O \tag{11}$$

$$Al_2O_3 + 4Ca(OH)_2 + 10H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 18H_2O \tag{12}$$

These equations show that if active silica and alumina react with lime, calcium silicate and calcium aluminate hydrates are formed. These compounds are similar to those that give strength to portland cement. The ability of a siliceous or aluminous material to react at normal temperature as shown is called "pozzolanic activity" and is measured by ASTM Method No. C 311-77 (11). A sufficient degree of pozzolanic activity may be present in spent shale or it may be increased by heat treatment, or by modifying retorting conditions, or by lime addition.

If pozzolanic activity could be induced in surface spent shale by modifying retort operating conditions, it may be possible to manufacture a hydraulic lime-pozzolan on site. This is more attractive than formation of a cement since activation of silica and alumina takes place at lower temperatures than the formation of clinker compounds (900 - 1000 C). For maximum development of cementitious properties, additional lime may be required. This could be added before retorting or afterward. Fine grinding of the spent shale would be required. Because the clinker compounds of portland cement, formed in equations (3) through (6), would not be present, the grout would set more slowly and have a lower final strength.

600 C to produce iron and magnesium oxides and calcite ($CaCO_3$). Calcite decomposes to calcium oxide and carbon dioxide between 700 and 950 C depending on the partial pressure of CO_2. Above 1000 C the calcium oxide reacts with silica to produce calcium silicate compounds ($3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$) and other nonreactive compounds (gehlenites and akermanites). These reactions are summarized as (12):

$$Ca(Mg_x, Fe_{1-x})(CO_3)_2 \xrightarrow{\Delta} (1-x)FeO + xMgO + CaCO_3 + CO_2 \qquad (13)$$

$$2FeO + CO_2 \xrightarrow{\Delta} Fe_2O_3 + CO \qquad (14)$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \qquad (15)$$

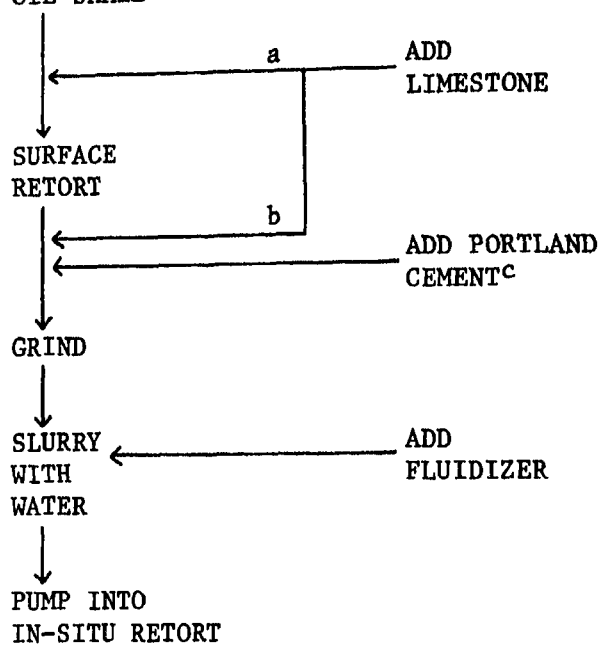$$nCaO + mSiO_2 \xrightarrow{\Delta} Ca_n Si_m O_{(n+2m)} \qquad (16)$$

The temperature at which these reactions occur is very important in considering the use of oil shale as a cementitious material. Most surface retorts operate at less than 600 C, which is too low to form a mixture of active silica and active alumina with cementitious properties. Therefore, if spent shale is to be produced for use as a grouting material, the surface retorting process may have to be optimized for pozzolan formation as well as for oil yield.

Based on the foregoing, we propose that the surface retort be operated to produce a hydraulic lime-pozzolan mixture. This recommended strategy is summarized in Figure 1. This figure shows pozzolan production and additives that are being explored in an experimental program. The surface retort is operated to produce a hydraulic lime-pozzolan. The effect of additions of limestone, portland cement and slurry fluidizer are being investigated. The limestone addition would enhance the availability of lime to form cohesive hydrates. If strength of the lime-pozzolan mixture is inadequate, a small addition of portland cement may be desirable. The portland cement would contribute tricalcium ($3CaO \cdot SiO_2$) and dicalcium ($2CaO \cdot SiO_2$) silicate, which, upon hydration, yield Ca(OH)$_2$ and cohesive hydrates. The spent shale pozzolan would react with the Ca(OH)$_2$ as it is formed to yield additional cohesive hydrates as shown in equations (11) and (12). The slurry fluidizer would decrease the viscosity of the slurry so that it could be more easily distributed in the abandoned retort.

GROUT DISTRIBUTION

Grout distribution in abandoned retorts will depend on several factors including grout properties, retort properties and emplacement geometry. Most commercial grouting is performed by point injection from small diameter pipes placed in a grid pattern on centers less than 20 feet apart. This would not be economically feasible due to the large number of deep holes that would have to be drilled. Well spacing greater than or equal to 70 feet

```
OIL SHALE
    │
    │◄──────────── a ────── ADD
    │                       LIMESTONE
    ▼
SURFACE
RETORT
    │◄──────────── b
    │◄──────────────────── ADD PORTLAND
    │                       CEMENT c
    ▼
GRIND
    │
    ▼
SLURRY ◄──────────────────── ADD
WITH                         FLUIDIZER
WATER
    │
    ▼
PUMP INTO
IN-SITU RETORT
```

[a] Add limestone before retorting if retorting temperature is high enough to calcine limestone.

[b] Add calcined limestone after retorting if retorting temperature is not high enough to calcine limestone.

[c] Portland cement addition only if strength development without it is inadequate.

of the grout emplacement, the retort permeability and grout viscosity on retort groutability need to be studied.

Viscosity is the most important grout property for distribution. Spent shale slurries investigated to date have typically had viscosities of 500 to over 1000 cp at low water contents (100% by weight water added) (6). These slurries have generally had viscosity reduction to 50 cp at 200% by weight water added but some slurries have required 1000% by weight water to obtain viscosities less than 100 cp (for comparison, the viscosity of water is 1 cp at 20 C). The relative penetrability of spent shale grout will be strongly dependent on obtaining a low viscosity product (< 50 cp) at low water content (100% by weight water) to achieve desired strength development and permeability reduction.

Permeability of the spent in-situ retort will be the most important property for grout distribution. Uniform penetration of a particulate grout (e.g. spent shale-based grout) may be difficult to achieve because of the heterogeneous nature of the void space of an abandoned in-situ retort. It includes large voids between rubble fragments (up to one inch and more), fine voids where oil shale has been fractured but fragments have not moved apart, fissures and cracks in retort walls, and minutes pores created in spent shale by pyrolysis of kerogen. Invasion of only the larger pores may not be adequate to reduce permeability.

Effective grouting may require complete and uniform penetration of most voids. This will be controlled by the relative size of particles in the grout and the void space in the rubble. In order to penetrate a retort at a reasonable pressure and flow rate, the size of the largest suspended particle should not be greater than about one-third of the size of the voids. Typically, particulate grouts are used for openings that are 1/16 inch or larger and chemical grouts are used for openings that are less than 1/16 inch. Therefore, two injections may be required to seal an abandoned in-situ retort. The first would use a grout with a relatively large particle size and the second would use a nonparticulate grout.

Point source grout injection may not be very effective for grout distribution in abandoned retorts. The grout penetration from a point source is severely limited by the high headloss developed near the tip of the pipe. For most commercial grouts however, set up time is short and point sources are used because not enough grout penetration occurs prior to set up for the well point headloss to become a problem. However, for abandoned retorts, this configuration is not suitable as a large number of injection ports would be required. The cost for this may be excessive. Therefore, line source placement should be explored.

Line source injection is beneficial for increased rubble penetration and faster grout distribution but it is limited by the size of the pipe available to deliver the grout and head required to push the grout through the rubble. A 36 inch pipe diameter flowing at 2 ft/sec could deliver 14 cfs of grout to the rubble. If this grout were delivered to a slotted section approximately 50 feet in length, approximately 8 hours would be

This paper considered the production of a hydraulic lime-pozzolan mixture from spent shale produced in surface oil shale retorts. This mixture could be slurried with process effluents and pumped into abandoned MIS retorts. This control strategy would simultaneously provide for long-term retort stability, minimal groundwater disruption, enhancement of resource recovery and disposal of process residuals. Work completed to date and some theoretical considerations suggest that surface retorts can be operated to produce a spent shale with pozzolanic properties. Additions of limestone, portland cement and slurry fluidizer may be required. Additional work is required to determine optimum retort operating conditions and required additives, and to resolve a number of technical problems. Preliminary cost estimates indicate that this would be an economically viable strategy if technical issues could be resolved. These include high grout viscosities, high water-solid ratios, poor strength development and grout distribution within an abandoned retort. If spent shale grout or some other low-cost on-site waste material cannot be reclaimed for retort filling and plugging, it is possible that MIS retorting may not be both environmentally and economically viable due to the high costs associated with other control strategies. However, if the constraint of enhanced resource recovery is relaxed and if it can be demonstrated that creep and subsidence are not long-term problems, then other lower-cost control strategies may be considered. These would address only the groundwater disruption issues and would include leaching, mine design modifications, grout curtains, and chemical immobilization of leachables.

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ABSTRACT

The injection of wastes into deep underground formations is the most economical method for disposal of liquid wastes that are not amenable to surface treatment. Operating costs are lower for pretreatments and subsurface disposal than for surface treatment systems, and plant area requirements are fewer. Chemical treatment is minimal, and generally the only physical treatment required for underground injection is filtration. This report presents a broad view of modern industrial underground waste injection systems and their operations. The types of wastes being injected and the major features of equipment, geologic formations, and well operation are described.

The petroleum industry has been injecting fluids into subsurface formations for many years; therefore, many of the techniques and much of the equipment for handling industrial liquid wastes are already available for industrial waste disposal. The techniques for drilling and completing the disposal wells have been perfected, and the necessary equipment is available. Similarly, the behavior of fluid flow through porous rocks and unconsolidated sand has been investigated. Therefore, many of the theories and equations describing the fluid distributions have been proved. Modificaton may, however, be needed to make them applicable to waste injection systems and to describe the chromatographic properties of the injected wastes constituents.

A subsurface disposal system can be successful only if a porous, permeable formation of wide areal extent is available at sufficient depth to ensure safety in storage and retention of the injected fluids. The wastes usually are treated for solids removal and compatibility with the formation. An impermeable zone, such as shale or evaporite, must overlie the injection horizon to prevent vertical migration of the waste or displaced formation brines into low-salinity aquifers above the disposal zone.

This report presents a broad view of modern industrial underground waste-injection systems and their operations. The types of wastes being injected and the major features of equipment, geologic formations, and well operation are described.

Almost any specific waste-disposal problem can be resolved with modern industrial technology, but the processes for waste treatment and disposal are limited by practical economics. The injection of liquid wastes into deep geologic formations is becoming increasingly important. This method is being used especially in the major oil-producing states, where the technology of fluid extraction from, and injection into, underground formations was developed and has been in use for about 50 years.

The experience of the petroleum and chemical industries has shown that underground injection is applicable to all types of liquid wastes, (e.g. mineral and organic acids, bases, inorganic salts, oxygenated and chlorinated hydrocarbons, and mixtures of many other types of compounds).

Subsurface formations have extremely large adsorptive surfaces and contain a diverse population of anaerobic bacteria; both of these factors are beneficial in containing and decomposing the injected wastes. In addition, salts contained in subsurface brines and the diverse chemical constituents of host rocks serve as buffering agents and chemical reactants to aid in the conversion and decomposition of the waste compounds.

If deleterious waste compounds are, indeed, irreversibly adsorbed and decomposed to harmless compounds, the environmental impact of underground waste storage is significantly less than that of chemical waste disposal by burning or discharging to surface streams or the ocean. However, present limitations of knowledge of the possible reaction of waste constituents with subsurface formations impose a potential for creation of an environmental hazard.

TYPES OF WASTES

The selection of subsurface waste disposal as a means of disposing of wastes is based on: (1) the difficulty of treating the waste to an acceptable level of purity for reuse or for discharge to surface streams and (2) the economic margin, if any, between subsurface waste disposal and surface treatment methods.

Some wastes are corrosive acidic or brine solutions of inorganic constituents; some are basic wastes that readily form insoluble hydroxides and other precipitates when mixed with other

considered. Thus, each system is unique, because it must be designed to process a specific waste mixture for injection into a particular geologic formation.

In this report, the types of wastes being injected into underground formations are classed in three distinct categories: produced oilfield brines, inorganic industrial wastes, and organic industrial wastes, as shown in Tables 1, 2, and 3, respectively. Each of the three types of wastes is subdivided on the basis of the individual waste constituents or of some outstanding property such as pH.

Oilfield Brines

In some oil fields being produced by waterflood, the brine produced with the oil is reinjected into the oil-producing formation for displacement of crude oil. Thus, the brine that would otherwise be a waste product is used for additional oil recovery and economic gain. Additional quantities of water required for a waterflood project are usually obtained from brine wells completed in formations above or below the oil zone.

However, just as many oil fields are being produced by other mechanisms that do not require the injection of brine into the oil-producing formation. In these fields the produced brine is a waste product which is disposed of by injection into subsurface formations from which no fluids are withdrawn. Thus, this operation is similar to the injection of liquid wastes by the chemical industry.

Oilfield brines have a wide range of concentrations of a large variety of cations and anions. Concentrations range from less than 100 ppm to more than 100,000 ppm, as shown in Table 1, where the brines are classified according to the cation and anion in greatest concentration. Most of the produced brines have sodium or calcium chlorides as their major constituents, but magnesium, bicarbonate, and sulfate ions predominate in some. Other ions are present as minor constituents, and in some brines, ions such as bromine and iodine are present in commercially economic quantities (5).

Concentrations of ions from waters of different geologic formations, and in places even at different sites within the same formation, differ widely. Consequently, there are no typical oilfield brines, and generalizations of the chemical reactivity of different brines cannot be made. However, some problems

TABLE 1. – Analyses of Natural Groundwaters Showing Major
Constituents of Various Types of Brines (ppm)

Type of Brine	Formation	Location	Na	Ca	Mg	Cl	HCO$_3$
Sodium chloride	Big Injun	Pa.	52,200	1,730	3,910	121,000	70
Sodium carbonate	Ellis	Mont.	3,140	90	80	2,890	4,040
Sodium sulfate	Coalinga	Calif.	3,290	390	340	2,520	360
Calcium chloride	Arbuckle	Kans.	4,230	16,900	8,430	60,100	42
Calcium carbonate	Embar	Wyo.	140	140	30	10	210
Calcium sulfate	Madison	Wyo.	580	870	180	1,070	1,080
Magnesium chloride	Lodgepole	Manitoba	44,900	3,260	67,340	94,900	2,140
Magnesium carbonate	Uinta	Colo.	450	428	542	90	1,185
Magnesium sulfate	---	New Mexico	100	1,000	25,000	9,000	0

1. **Precipitates**: Unless the brines are processed in a closed system, atmospheric oxidation of brine constituents causes the precipitation of salts and hydroxides. Complete removal by filtration is too costly; therefore, aeration equipment is used to complete the oxidation, which is followed by sedimentation and filtration.

Closed systems are used to keep the brine in essentially the same condition that existed in the formation. The closed system is more economical to operate and requires less surface equipment than the open system because the need for aeration and sedimentation is eliminated. Brine is removed from the oil-water separator, filtered, and pumped directly into water wells. Closed systems generally are used where brine is to be injected into a formation other than the oil-producing formation, as a waste-disposal method.

2. **Scale deposition**: Crystals from the concentrated salt solutions tend to accumulate in pipelines and at the face of the formation. They restrict the flow of brine and increase pumping costs. Such scale deposits are controlled by the addition of chemicals, principally phosphates, to the brine at the injection-pump manifold.

3. **Corrosion**: Brines containing dissolved oxygen are very corrosive to ferrous metals. The phosphates added to prevent scale deposition act also as mild corrosion inhibitors, and usually no other corrosion-inhibiting chemicals are added to the brines. However, the corrosiveness of some brines, such as those containing carbonates, may be so great that corrosion inhibitors must be added to prevent loss of surface pipes.

Inorganic Industrial Wastes

Analyses of the inorganic wastes of 18 companies are listed in Table 2 to illustrate the wide variety of chemical-process waste mixtures and to show the stark differences between these wastes and oilfield brines. These wastes have been classified as essentially neutral, basic, or acidic. The neutral wastes, which are low in dissolved organic compounds, are more similar in chemical behavior to oilfield brines than are the others.

The only preinjection treatment required for many of these neutral salt solutions is filtration. However, wastes containing dissolved organic compounds usually complicate underground injection by forming polymeric gums at the formation face and in pores near the well bore.

TABLE 2.--Inorganic wastes that are being injected into deep geologic formations

No.	Description of waste	Injection rate, gpm	Injection pressure, psi	Depth of Well, ft	Description of formation
	Neutral Wastes				
1.	NH_4Cl (15,000 ppm); NaCl (1,600 ppm); $CaSO_4$ (260 ppm); Na_2CrO_4 (40 ppm); $ZnCl_2$ (5 ppm); urea (4,000 ppm)	900	200	900	Limestone - vugular
2.	$(NH4)_2SO_4$ (32%); NaCl (1.5%); nitriles (0.07%) BOD = 10,000 ppm; pH = 6.7	1,000	500	7,000	Sandstone, 700' thick, $\emptyset$ = 28%; k = 300 md
3.	Na_2SO_4 (800 ppm); NaCl (300 ppm); NaF (20 ppm); $NaNO_3$ (3 ppm); $FeCl_3$ (2 ppm); $MnSO_4$ (2 ppm); $ZnCl_2$ (5 ppm); phenols (500 ppm); detergents (300 ppm); pH 7.9, BOD = 50 ppm	50	0	3,000	Limestone - vugular
4.	Na_2SO_4 (2,000 ppm); Na_3PO_4 (10 ppm); $FeCl_3$ (800 ppm); $NaNO_3$ (100 ppm); Na_2CrO_4 (10 ppm); pH = 7.5	80	0	3,800	Dolomite - vugular
5.	NaCl (1,800 ppm); $CaCO_3$ (400 ppm); $MgCO_3$ (400 ppm) $(NH_4)_2SO_4$ (1,500 ppm); hydrocarbons (1,500 ppm); pH = 8.0	50	400	1,100	Unconsolidated sand; $\emptyset$ = 32%; k = 2,000 md
	Basic Wastes				
6.	NaOH (3.0%); Na_2SO_4 (1.0%); Phenol (1.0%); acetone (0.2%); pH = 12	100	300	6,500	Sandstone with beds of sand, gravel and clay. k = 200-1,000 md, $\emptyset$ = 28-32%.
7.	NaOH (7.5%); Na_2S (1.2%); Na_2CO_3 (2.2%); Na_2SO_4 (0.7%); NaCl (0.3%); Phenols (0.5%); mercaptans (0.4%); pH = 9.4; BOD = 5,000 ppm	350	400	6,950	Unconsolidated sand, 250' thick
8.	NaOH (1.5%); Na_2CO_3 (5.4%); NaCl (13.1%); Glycerine (5.0%); Epichlorohydrin (4.6%); Epoxy resin (1.9%); Phenol (3.2%); acetone (1.6%); pH = 11.2	150	200	6,200	Sandstone with beds of sand, gravel and clay. k = 200-1,000 md, $\emptyset$ = 28-32%.

TABLE 2.—Inorganic wastes that are being injected into deep geologic formations (cont.)

Description of waste	Injection rate, gpm	Injection pressure, psi	Depth of Well, ft	Description of formation	Years in Operation
(395 ppm); NaCl (9,100 ppm); CaSO4 ... ppm); Mg SO4 (1,500 ppm); NH3 ... ppm); adipic acid (1,500 ppm); ... e organics (1,000 ppm); pH = 8.5. ... HCl (6.0%) and HNO3 (4.0%) are added ... e injection pump manifold.	1,100	1,000	5,800	Limestone, vugular, with sand inclusion in some areas. ∅ = 18%, k = 5 md.	6
4.0%); NaF (2.8%)	50	150	4,300	Unconsolidated sand	2
5,000 ppm); NaCl (32,000 ppm); hydrocarbons- ... urated (1,500 ppm); pH = 10; COD = 3,000	200	100	7,200	Unconsolidated sands containing shale and clay; ∅ = 27; k = 1,000 md	3
Wastes (7.0%); Na2SO4 (3,000 ppm); CaSO4 (800 ppm); ...O4)3 (700 ppm); CrSO4 (150 ppm) acetic acid ... ppm); pH = 1.0	100	300	3,800	Unconsolidated sand alternating with shale, 1,500' thick, ∅ = 20%, k = 1,200 md.	2
.1%); FeCl2 (1.8%); FeCl3 (1.5%); pH = 2	100	50	4,200	Unconsolidated sand, containing clay and shale, k = 1,500 md, ∅ = 32%	1
SO4 (0.2%); H2SO4 (0.2%); HNO3 (50 ppm) ...ic acids (50 ppm); Nitriles (100 ppm), 2.5	350	100	4,500	Unconsolidated sand, 800' thick, ∅ = 32; k = 1,500 md	2
9.3%); Na2SO4 (27.7%); H2SO4 (7.8%); HCl ...); H2O2 (2.7%); Organic acids (4.7%); Org. ...ides (3.3%); alcohols (1.9%); ketones (1.1%)	30	750	3,700	Sandstone containing chalk. k = 10-1,000 md, ∅ = 20-25%	3
.1%); FeCl2 (23.4%)	150	0	2,300	Sandstone, ∅ = 12%, k = 100 md	6
(8.5%); FeSO4 (13.0%)	150	0	2,300	Sandstone, ∅ = 12%, k = 100 md	6
2.0%); H2SO4 (2.0%); NaCl (10%); acetic ...(2.0%); chloroacetic acid (1.0%); ...inate hydrocarbons (0.5%)	200	0	4,000	Limestone, vugular	12

TABLE 3.--Organic wastes that are being injected into
deep geologic formations

No.	Description of waste	Injection rate, gpm	Injection pressure, psi	Depth of Well, ft	Description of formation
	Aldehydes				
1.	Chlorinated aldehydes (1.9%); acetic acid (1.3%); acetaldehyde (0.3%); pH = 5	200	500	5,400	Unconsolidated sands ranging in thickness from ft, separated by thin shale beds; $\emptyset$ = 30-40%;
2.	Formaldehyde (0.4%); acetaldehyde (0.4%); Butyonaldehyde (0.3%); crotonaldehyde (0.2%); methyl alcohol (0.2%); butyl alcohol (0.14%); acrolein (0.02%); formic acid (0.01%); acetic acid (0.01%)	850	600	4,500	Unconsolidated sand; $\emptyset$ = 30-40%; k = 1.0-3.0 Da
3.	Acetaldehyde (750 ppm); propanol (100 ppm); acetone (350 ppm); acrolein (100 ppm); butanol (150 ppm); methyl ethyl ketone (300 ppm); vinyl methanol ketone (600 ppm); cyclobutanone (600 ppm); dioxane (100 ppm); NaCl (5,000 ppm); NaHCO3 (1,000 ppm); pH = 7.3	800	0	4,000	Sandstone and detrital granite; $\emptyset$ = 25%; k = 50
	Alcohols				
4.	Hexanol (0.10%); amyl alcohol (0.06%); methanol (0.02%); dibasic acids (0.82%); hexamethylene imine (0.14%); cyclohexane (0.02%); dodecane (0.01%); NaNO3 (1.3%); NaHCO3 (0.35%); unidentified organics (2.40%); pH - 9.1	250	450	3,300	Loosely consolidated sand, 260 ft thick. $\emptyset$ = 3 k = 1.0 - 2.0 Darcy.
5.	Polyvinyl alcohol (300 ppm); methanol (1,400 ppm); acetic acid (400 ppm); hydroquinone (100); silicones (23 ppm); vinyl acetate, (1,200 ppm); methyl acetate (800 ppm); acetaldehyde (500 ppm); ethyl acetate (50 ppm); sodium acetate (2,300 ppm); pH = 5	250	500	7,000	Sandstone interbedded with shale.

TABLE 3.--Organic wastes that are being injected into deep geologic formations (cont.)

No.	Description of waste	Injection rate, gpm	Injection pressure, psi	Depth of Well, ft	Description of formation
	Glycols				
6.	Ethylene glycol (1.0%); K$_2$CO$_3$ (1.0%)	350	350	5,000	Unconsolidated
7.	Ethylene glycol (500 ppm); propylene dichloride (125 ppm); propylene glycol (11,000 ppm); acetone (40 ppm); ethylene dichloride (1,200 ppm); dichloroisoproyl ether (90 ppm); dichloroethyl ether (40 ppm); NaCl (5%); Na$_2$SO$_4$ (0.05%); Na$_2$CO$_3$ (0.01%)	300	300	6,000	Unconsolidated sand.
	Phenols				
8.	Phenols (6.2%); cyanides (1.2%); ammonia (0.3%); thiocyanides(0.1%); NaCl (0.3%)	100	0	1,800	Sandstone, k = 200 md. Ø = 15%
	Acids				
9.	Acetic acid (0.5%); chloroacetic acid (0.4%); acetaldehyde (0.1%); acetaldol (0.1%); Butanol (0.05%); crotonaldehyde (0.05%); NaCl (0.5%); pH = 2.5, COD = 29, 400 ppm; BOD = 9,900 ppm.	350	400	3,500	Unconsolidated sand. Ø = 27-35%; k = 0.5-2 D
10.	Adipic acid (8%); caprolactam (1%); butanol (0.5%); benzene (0.2%); cyclohexane (0.3%); NaCl (2%)	100	350	6,000	Sandstone, k = 0.2-1.0 Darcy, Ø = 28%
11.	Organic acids (dibasic - principally adipic) (2.6%); nitric acid (0.8%)	400	200	5,200	Loosely consolidated sand.
12.	Acetic acid (3,000 ppm); paratoluic acid (100 ppm); benzoic acid (50 ppm); xylene (100 ppm); methyl ethyl ketone (50 ppm); CaCl$_2$ (200 ppm); MgSO$_4$ (200 ppm); pH = 3.0	200	400	6,000	Sandstone, Ø = 30%; k = 500 md

No.	Description of waste	Injection rate, gpm	Injection pressure, psi	Depth of Well, ft	Description of formation
13.	C_2-C_6 organic acids (6,700 ppm); C_1-C_4 alcohols (2,000 ppm); C_1-C_3 ketones (1,400 ppm); propylene glycols (400 ppm); propyl esters (2,000 ppm); propylene oxide (3,000 ppm); C_5-C_6 hydrocarbon (2,000 ppm); Na_2SO_4 (2,000 ppm); NaCl (500 ppm)	400	800	7,000	Sandstone; $\emptyset$ = 27%; k = 300 md.
14.	Acetic acid (160 ppm); maleic acid (100 ppm); xylene sulfonic acid (50 ppm); benzoic acid (50 ppm); butyl alcohol (950 ppm); styrene (100 ppm); isoproponal (100 ppm); phthalic acid (100 ppm); methyl ethyl ketone (250 ppm); NaOH (300 ppm); H_2SO_4 (500 ppm); Na_2CO_3 (350 ppm) (650 ppm)	250	1,200	7,200	Sandstone containing beds of clay; k = 200 md; $\emptyset$
15.	Nitriles Glycol nitrile (0.5%); iminodiacetonitrile (0.3%); nitrilotriacetonitrile (0.2%); other organic nitriles (1.0%); methanol (0.1%); methyl formate (0.1%); formaldehyde (0.3%); formic acid (0.5%); H_2SO_4 (1.7%); $(NH_4)_2SO_4$ (4.3%)	150	200	6,500	Sandstone, 400 ft thick, $\emptyset$ = 28%; k = 200 md.
16.	Disulfides Ethyl disulfide (30%); propyl disulfide (40%); butyl disulfide (25%); mercaptans (5%); water insoluble oil	5	0	2,200	Unconsolidated sand with thin clay beds, 100-ft
17.	Ethyl disulfide (4%); propyl disulfide (6%); butyl disulfide (14%); pentyl disulfide (14%); hexyl disulfide (3%); NaOH (8%)	10	60	1,500	Vugular limestone

lems in addition to the three major problems associated with disposal of oilfield brines. Pore spaces near the well bore can quickly become plugged. Insoluble salts of metals in the waste can be deposited in the pores, or hydroxides of metals may form gels that effectively plug the pores. Resinlike materials, such as the epoxy resin in Waste 8 (Table 2), may polymerize in the formation and plug the pores.

Waste mixtures may also react with clay minerals such as montmorillonite and illite (14), found in most sedimentary rocks, causing the clay to swell and reducing the permeability of the formation. This problem is especially troublesome with dilute neutral wastes. Reactions of components in the waste with formation brine or constituents of the formation matrix may cause the evolution of gas, which can produce high pressures and loss of permeability near the well bore.

Where the degree of incompatibility between the formation brine and waste is high, a large volume (200,000 to 500,000 gal) of a nonreactive fluid can be injected ahead of the waste to act as a buffer between the two incompatible fluids. The degree of mixing in the formation between the injected fluid and native brine is relatively small. Mixing occurs in a thin transient zone, and its rate, quantity, and adverse effects depend on the chemical and physical properties of the native brine, the formation, and the wastes. It is only when this mixing occurs in or near the well bore that severe problems arise. The nonreactive buffering fluid injected in front of the waste moves the mixing zone in the formation far away from the well bore so that incompatibility is no longer an adverse factor.

Because inorganic acidic wastes are highly corrosive, they present additional problems of acceptability for underground injection. Corrosion of surface equipment and well components can cause plugging of the formation from the insoluble reaction products. If corrosion can be minimized and initial incompatibility problems eliminated by developing a buffer zone of nonreactive fluid, the injection of low-pH wastes proceeds with ease, regardless of the type of formation selected for injection.

As injection proceeds, the permeability of the formation gradually increases. This fact was demonstrated with rock core samples in the laboratory experiments of Champlin and co-workers (4). They injected a simulated acidic waste into several outcrop cores and examined the physical properties of the sandstone cores before and after injection of the acidic solutions. In every

(1) solution, (2) displacement of some particles which were loosely bound with cementing materials, and (3) degradation of particles such as clay.

The success that the steel companies are having with the injection of waste pickle liquor (2) into the Mount Simon Sandstone is a good practical example of the injection of highly corrosive acidic wastes. Wastes 16 and 17 of Table 2 are two types of waste pickle-liquor hydrochloric and sulfuric acid, respectively. They contain a high load of iron that amounts to as much as 20 tons/day when injected at the current average rates. The wells disposing of these acidic wastes have been in operation for more than 15 years.

Acidic wastes are also being successfully injected into limestone and dolomite formations (6,7,8). Reactions of these acids with the carbonate formations have not caused adverse permeability problems, perhaps because the carbon dioxide formed by the reaction is sufficiently soluble in the waste and formation brines to be removed from the vicinity of the well bore by the fluid entering the formation.

Organic Industrial Wastes

The analyses of 15 waste mixtures that are aqueous solutions of organic waste constituents, many of which contain dissolved inorganic salts, are divided in Table 3 into categories that are most descriptive of the mixtures. The disulfide wastes (16 and 17 of Table 3) are water-insoluble oils that are being injected successfully without any attempt to make them water soluble.

The aldehydes, phenols, and nitriles have in common a marked tendency to form water-insoluble gums at the face of the disposal formation. Wells injecting such wastes must be stimulated periodically. Acidizing with a mixture of hydrochloric and hydrofluoric acids is the most common treatment, but it commonly is necessary to remove well tubing and reenter the well with drilling tools to remove the accumulation of gum from the formation face. Hydraulic fracturing, induced by pumping liquid in at high pressure until the strata are ruptured, is also employed for stimulation of wells completed in consolidated sandstone or carbonate rock.

The only other troublesome wastes listed in Table 3 are those containing low-boiling-point components that are irritants to the skin and mucous membranes, or are toxic. Wastes 2 and 3 contain acrolein, and Waste 9 contains chloroacetic acid; both

Aqueous fluids scheduled for injection into subsurface strata must be free of suspended solids, oil, and gas. The solids create a restriction to flow at the face of the formation, commonly called the "skin effect," and the oil and gas decrease the permeability to the aqueous phase by competing for the flow channels. Therefore, the objective of preinjection treatment of wastes is to remove solids, oil, and gas, or to stabilize a waste that may have a tendency to form a second phase during injection.

The selection of surface equipment depends on the physical and chemical properties of the waste and on the reservoir characteristics of the formation that has been selected for storage. The least complex systems are those designed to process wastes that are noncorrosive and free of suspended solids. The surface equipment required to process this waste includes: (1) a collecting tank; (2) transfer pipes; (3) an injection pump, if surface pressure is required for injection at the maximum flow rate of the waste; and (4) controls, such as float valves and recorders. There are a few such simple installations, but they are not typical because most industrial wastes cannot be injected into subsurface formations without previous treatment at the surface.

Waste from a chemical plant is generally a mixture of several waste streams from separate manufacturing units, cooling-tower blowdown, laboratory sinks, etc. Hence, the waste-disposal system begins with a sewer line that delivers the waste composite to a collecting reservoir of sump. The simplest sump is a cement sump placed several feet below the surface to allow gravity drainage. If the sump has a retention time of less than 1 hour, sedimentation of suspended solids will not occur to a large degree, and only an occasional raking of the sediment will be required. If a longer retention time is required in the sump, an automatic raking device usually must be installed to prevent sludge accumulation.

Waste-collecting ponds up to 2 million gallons in capacity and lined with an impermeable material may be used. Such large ponds are used to provide a long retention time and also to allow for mixing of the wastes by convection. Hence, these ponds are used where the wastes comprise several waste streams of different composition. A great disadvantage to large ponds with long retention times is the growth of bacteria and algae.

range. The pH also must be controlled if suspended solids must be removed by coagulation and sedimentation. Some wastes contain too much suspended solids for economical filtration, and the solids will not settle in sedimentation tanks without the aid of coagulants. Coagulants are also used where the disposal formation has very small pores, because the pores will be plugged by fine suspended solids that cannot be removed efficiently by filtration.

The size and type of injection pump to be installed are governed by the wellhead pressure, the volume of fluid, and the necessary rate of injection at peak loads. A few installations do not require an injection pump because the hydrostatic pressure of the column of waste in the disposal well exerts sufficient pressure at the subsurface face of the formation to inject the waste. If the wellhead pressure for waste injection is less than 150 psi, simple single-stage centrifugal pumps can be used; but, at higher pressure, multiplex piston-type or multistage centrifugal pumps are needed. Hence, selection of an injection pump must be delayed until the disposal well is ready for operation, and pumping tests can be made.

Some requirements for surface equipment and pretreatment of waste can be determined by testing the waste and the water of the disposal formation. Results of such tests will indicate the compatibility of the formation water and waste, and are useful in determining the treatment required. Even though compatibility can be determined in the laboratory, conditions as they exist underground are difficult to duplicate. A laboratory mixture of the two fluids that apparently is satisfactory may be incompatible in the subsurface, or the opposite may be true. Bernard (3) made some studies by pumping water solutions into sandstone samples that contained incompatible interstitial solutions. He did not observe a decrease in permeability that would have indicated plugging.

Because of the diverse nature of chemical wastes and disposal formations, the surface equipment for a waste-injection system cannot be designed until the formation to be used has been examined. The wastes from chemical manufacturing operations also vary greatly in chemical and physical properties. Therefore, each injection system is unique because the surface equipment is designed to process a specific waste for injection into a specific local portion of a formation. The best way to discuss surface equipment is to cite several examples, ranging from the simplest to the most complex. Three examples selected from the lists of wastes in Tables 2 and 3 are used to illustrate the variety in design and operation of surface equipment.

Waste 18 of Table 2. The waste is a highly corrosive mixture containing hydrochloric acid as a major constituent. However, the waste mixture is not complicated with suspended solids or undissolved oils that would have to be removed before injection. In addition, initial injectivity tests showed that the geologic conditions permitted the waste to be injected into the disposal formation, a vugular limestone at a depth of 4,000 ft (1,220 m), at the maximum anticipated flow rate under gravity flow. No injection pump was needed to force the waste into the formation, and the absence of suspended solids eliminated the need for filtration. Only a collecting sump and a metering valve to control the flow of waste into the well were required.

A 6-in., steel-jacketed, polyethlylene pipe transports the waste from the control valve to the wellhead, and the fluid pressure in this pipe is monitored. A light oil is maintained under pressure in the annulus of the well to support the fiber-cast tubing and to detect tubing leaks. A break in the tubing will cause an immediate change of pressure in the annulus.

The flow rate (averaged over a 30-day period) is 200 gpm with a slight vacuum at the wellhead and 35 psi pressure in the annulus. The average temperature of the waste at the wellhead is 120° F. Flow rates fluctuate from 450 gpm, which is in excess of the capacity of the well during periods of heavy rainfall, to a minimum of 110 gpm.

Closed System

A more complex system designed to process Waste 9 of Table 3 is illustrated in Figure 2. The waste is a water solution, very low in pH, containing hydrochloric acid, acetic acid, chloroacetal-dehydes, and chloroacetic acids. Although the organic concentration of the waste generally does not exceed 3% the low-boiling chlorinated hydrocarbon compounds make this a very reactive solution which is extremely irritating to mucous membranes and to skin. Therefore, this waste is handled in a completely closed system.

The selection of materials for construction of the surface equipment was a critical design consideration, because the waste is extremely corrosive to standard construction materials. Epoxy plastic pipe, Hastelloy C, 316 stainless steel, and titanium are used as required.
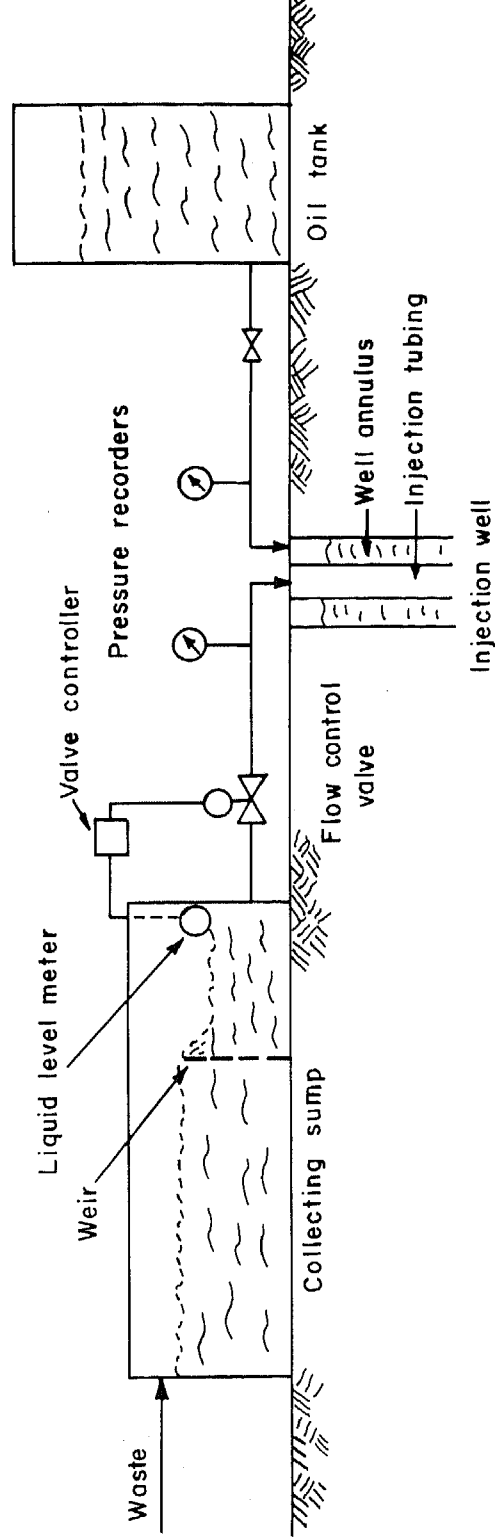
FIGURE 1.- Open Surface Equipment Used in One of the Simplest Waste-
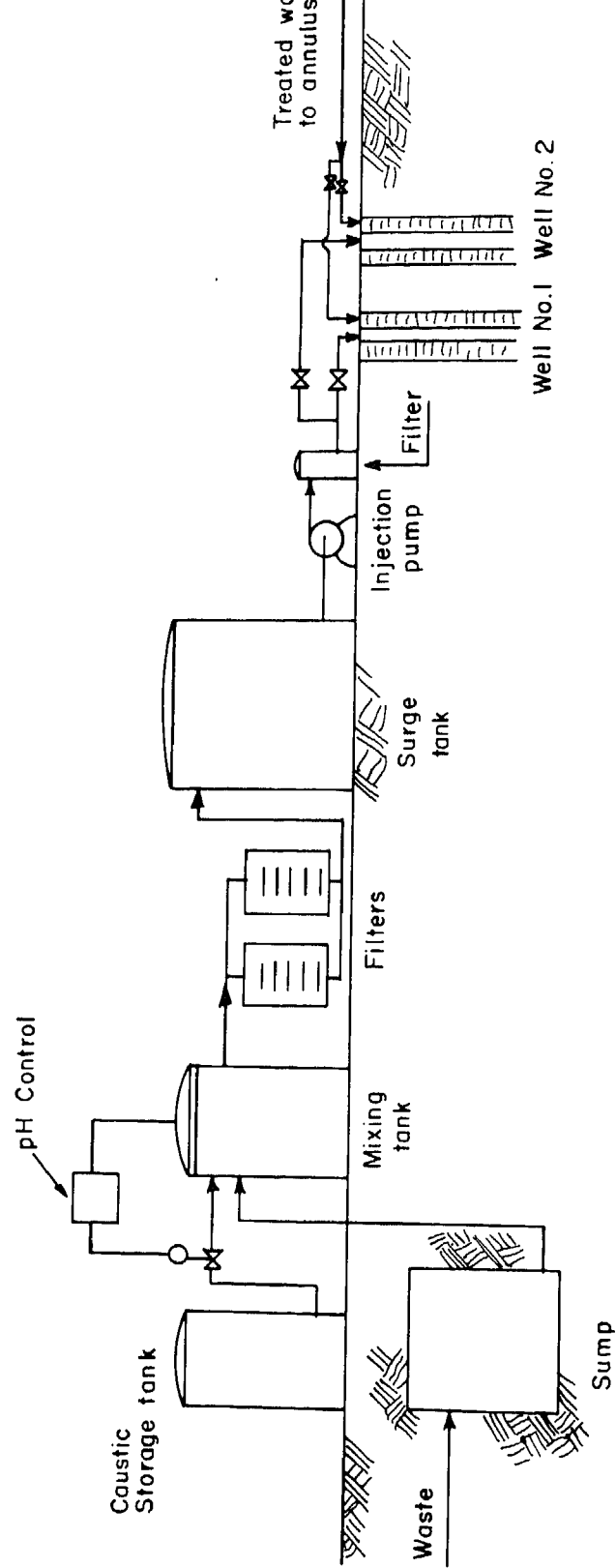Injection Systems.

FIGURE 2.— Closed Surface Equipment Used for Wastes Containing Volatile Organic Components.

4.0 and 5.0. The waste from the sump is not stable, forming polymers that precipitate upon standing, and, at a pH greater than 5.0, a tarlike polymer is formed by aldol condensation of the aldehydes.

Following pH control, the waste is filtered in rack-type pressure filters that are designed for backwash and precoat operation as completely closed systems. The processed waste is stored in a surge tank equipped with a liquid-level meter that controls the operation of the injection pump. As a final precaution, just prior to injection into one of the two wells, the waste is passed through a cartridge filter to remove any suspended solids that may have accumulated or formed during retention in the surge tank.

Two wells are maintained because the plant operation is completely dependent on the continued injection of the waste. There are no other provisions for disposal of this waste; hence, if only one injection well were used, failure of the well to receive the waste because of injection-tubing breakage, plugging, or other problems would result in complete shutdown of the chemical plant and considerable economic loss.

The annulus between the injection casing and the tubing is filled with boiler feed water which is reduced in pressure from 800 to 300 psi. The pressure of this fluid in the annulus is monitored continuously as a means of detecting tubing or packer leaks. Two single-stage centrifugal pumps connected in series are used to inject the waste at an average 350-gpm flow rate and 400 psi wellhead pressure.

Complex Open System

One of the most complex of the industrial waste-disposal systems is illustrated in Figure 3. It was designed to process Waste 9 of Table 2 for injection into a "tight" limestone. The waste contains a large load of suspended solids and some oil as it enters the collecting pond. The oil is skimmed from the surface with an automatic skimmer that travels slowly across the pond. The skimmed oil is burned in an incinerator. The waste then is treated with coagulators to accelerate sedimentation of the suspended solids, and with waste hydrochloric acid for pH control.

The sludge from the coagulator and backwash from the filters are sent to a drying bed, and the underdrain is returned to the collecting pond. A series of four leaf filters is used to filter the effluent from the coagulator, and the waste then is stored in
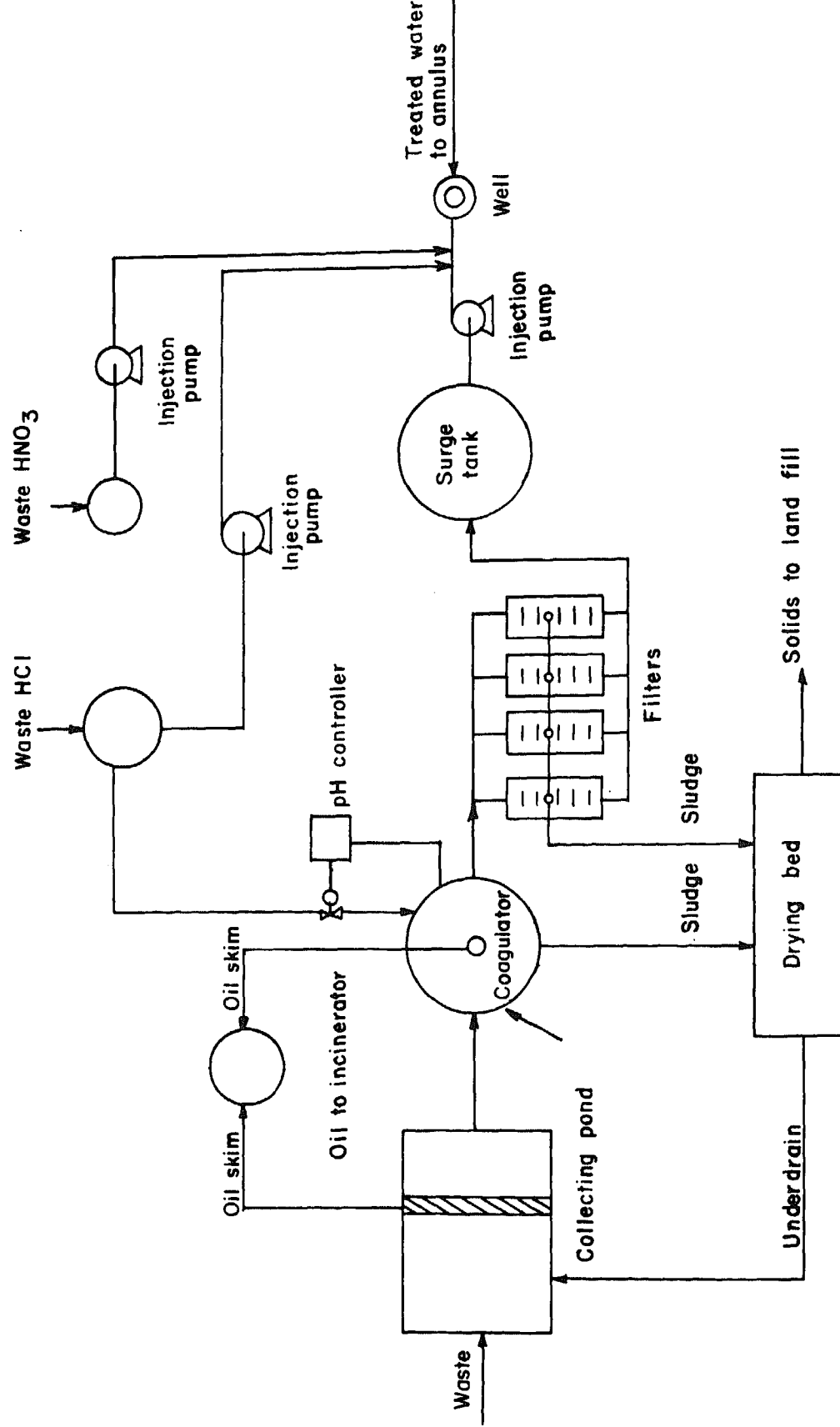
FIGURE 3.-Complex Open Waste Injection System.

streams are collected in separate tanks and pumped into the injection-pump manifold. The waste acids are collected separately because the waste streams are not constant; therefore, if the acids were added directly to the collecting pond, they would cause wide variations in the pH of the composite waste.

WASTE-INJECTION WELL DESIGN

Drilling and Casing

One of the most important criteria of a waste-disposal well is that it must be designed for complete protection of the near-surface, low-salinity aquifers through which the well is drilled. To accomplish such protection, a 12- to 18-in.-diameter hole is drilled to a depth at least 200 ft (60 m) below the deepest freshwater aquifer encountered. Surface casing (Fig. 4), at least 2 in. smaller than the hole diameter and equipped with centralizers, is run to the bottom of the hole. The annular space between the casing and the well bore is filled with cement. Experience with brine-injection wells has shown that this procedure will protect the freshwater aquifers from contamination if the injection casing is damaged.

After the surface casing has been installed, drilling is continued with an 8- to 12-in.-diameter bit through the potential disposal formations. Core samples of the potential disposal zones should be taken for laboratory examination, and the hole should be logged.

When a suitable disposal formation is selected, a 6- to 9-in.-OD string of casing - the injection casing - is centered in the hole, and cement is circulated to the surface in the annulus between the casing and the well bore (Fig. 4). The well is completed in the disposal zone by one of many methods, depending on the nature of the formation and the waste intended for disposal. Three of the most commonly used completion methods are illustrated in Figure 5.

Well Completion

If the formation is friable, indicating that the well bore may tend to cave and fill the bottom of the hole, a cased-hole completion technique (Fig. 5A) is used to provide positive support for the well-bore walls. For this type of completion, the hole is drilled to the bottom of the disposal formation, casing is set, and cement is circulated to the surface. The
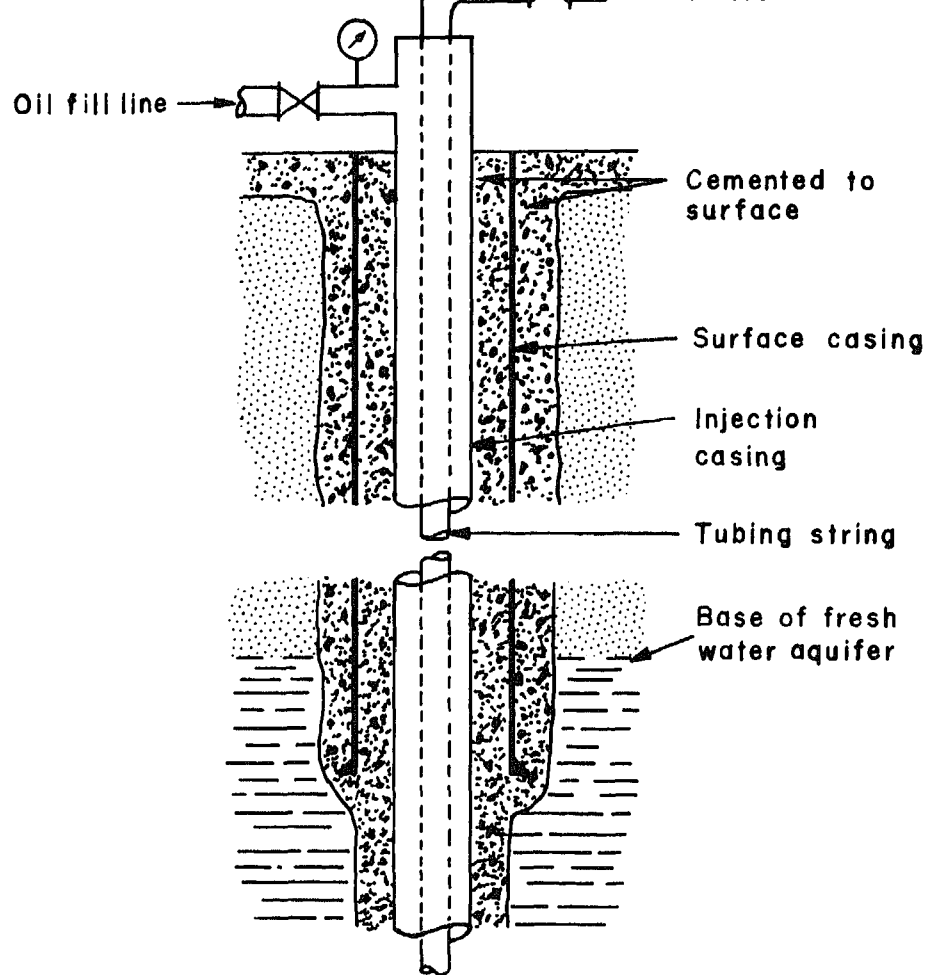
Oil fill line

Cemented to surface

Surface casing

Injection casing

Tubing string

Base of fresh water aquifer

FIGURE 4.-Waste-Disposal Well.

9-inch dia

7-inch O D

3½-inch O D

Packer

Cement

Gravel

Disposal f

Slotted lin
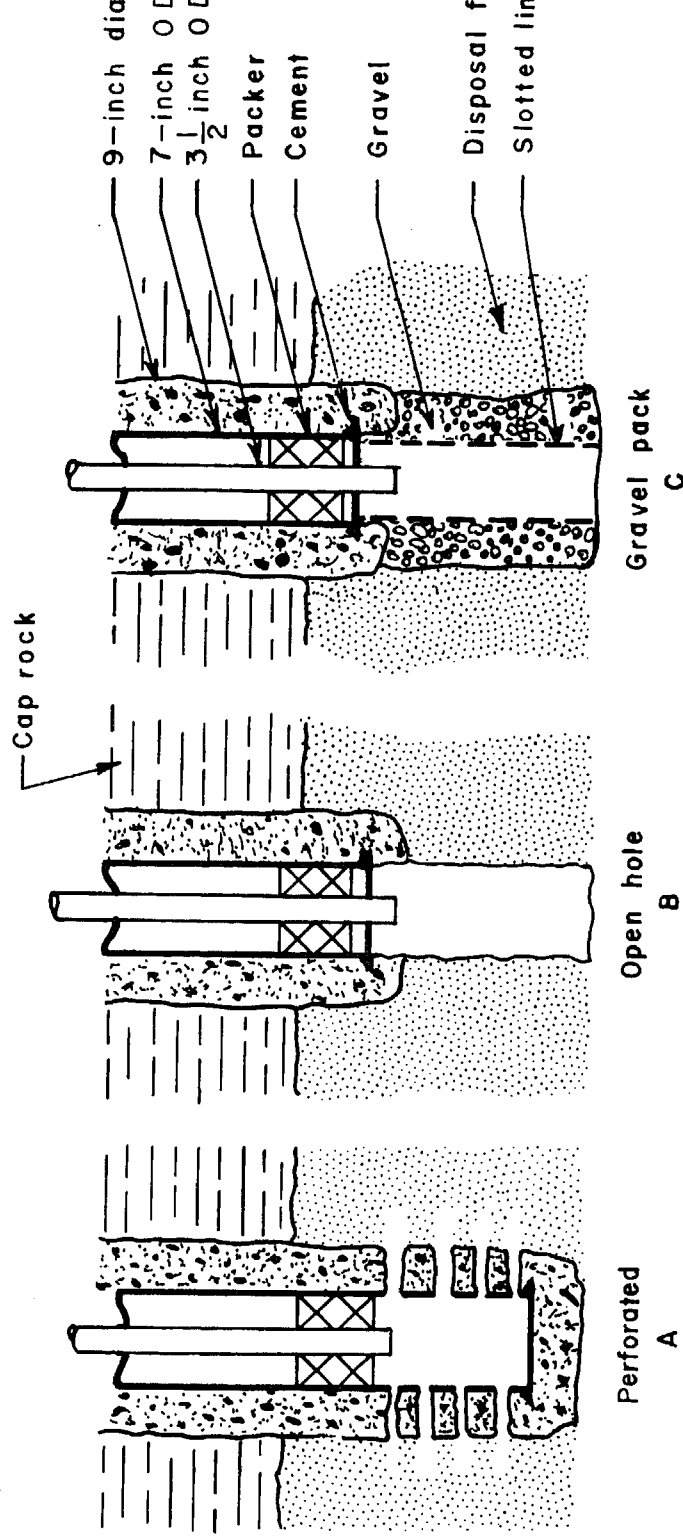
Cap rock

Gravel pack
C

Open hole
B

Perforated
A

FIGURE 5.-Disposal-Well Completion Methods.

zone, should be constructed of a corrosion-resistant alloy, such as stainless steel.

Where the disposal zone is a hard consolidated sandstone or a vugular carbonate formation, open-hole completion (Fig. 5B) may be used. Casing is set at the top of the disposal formation and cemented to the surface. Then an open hole is drilled to the bottom of the disposal zone. Open-hole completion also is used if corrosive wastes are to be injected, because products from corrosion of the casing in the disposal zone may plug the formation. Corrosion will also cause casing adjacent to the disposal zone to fail, allowing the cement to crumble and fill the hole with debris.

The third general type of completion, gravel pack (Fig. 5C), is used in unconsolidated sands to prevent sand from filling the bottom section of the injection casing or tubing, and thereby restricting the flow of the waste solution. The sand and gravel pack together at the bottom of the casing to form a tortuous path for the sand moving toward the well casing. The formation sand jams and movement stops; however, space for unrestricted liquid flow is left between the grains of sand and gravel.

Several other completion methods are used in unconsolidated sand. If the well is less than 2,000 ft (600 m) deep, air-lift valves may be installed in the annulus between the casing and tubing. Whenever sand restricts the flow of waste, the bottom section of casing can be cleaned of sand by blowing air through the tubing to lift the sand through the annulus. Another method is to perforate the casing with 1/10-in.-diameter pinholes adjacent to the sand formation (10). The sand may also be consolidated by treatment with epoxy plastic (11).

Sometimes the waste is injected directly through the injection casing, but this practice is inadvisable for corrosive waste, even with plastic-coated pipe, since absence of pinholes in the plastic coating cannot be guaranteed. The injection casing is best protected by use of an injection-tubing string inside the casing. Although some tubing strings made of corrosion-resistant metal alloys are used, the most popular material is a fiberglass-epoxy tubing, because of its high resistance to corrosive materials and its light weight.

Usually a packer is installed at the bottom of the long string of tubing in the annulus between the casing and tubing (Fig. 5). Additional protection of the injection casing is

pressure is immediately transmitted to a leak line and injection tubing.

A special type of completion is used in some of the wells designed for injection of waste steel-pickling liquor (Wastes 16 and 17, Table 2). A packer is not used at the bottom of the tubing to seal the annular space between the tubing and casing, as illustrated in Figure 5B; instead, electrodes are installed at the bottom of the tubing in the annular space. Water is pumped continuously into the annulus at a pressure slightly greater than the pressure of the waste in the tubing, allowing a constant flow of water through the annular space. The conductivity of water at the bottom of the tubing is monitored to detect accidental entry of acid into the annular space.

This brief discussion of well construction and completion is included only to show the principal features of design. A more complete presentation of the details of construction and procedures used in the construction of waste-disposal wells was given by Baker (1).

FORMATION CHARACTERISTICS

A subsurface-disposal system can be successful only if a porous, permeable formation of wide areal extent is available at sufficient depth to insure safety for storage and retention of the injected fluids. The stratum must be below all freshwater aquifers and confined vertically by rocks that, for practical purposes, are impermeable to waste liquids. In addition to the protection of usable water resources, the vertical confinement of liquid wastes also protects any developed or undeveloped hydrocarbon and mineral deposits.

Rocks that comprise the earth's crust are classified as igneous, metamorphic, and sedimentary. Of these, sedimentary rocks, particularly those that were deposited in a marine environment, are most likely to have good injection characteristics. Under favorable circumstances, however, both igneous and metamorphic rocks can have sufficient porosity and permeability to receive large volumes of liquid.

Some of the more suitable sedimentary rocks are sandstone, limestone, and dolomite. These rocks usually are porous and permeable enough to be used as injection zones. Naturally fractured limestones, dolomites, and shales may provide satisfactory injection horizons. However, the kind of rock most favorable for industrial waste disposal depends upon the chemical nature of the specific waste to be injected and should be determined for each disposal project.

are characteristics of many reservoirs could greatly complicate adequate containment and monitoring of injected fluids.

The injection zone must be isolated, both above and below, to prevent the vertical escape of injected waste. Unfractured shale, clay, slate, anhydrite, gypsum, marl, and bentonite have been found by the petroleum industry to provide good seals against the upward flow of oil and gas (13). The formation thickness required to confine liquid industrial waste cannot be rigidly established. A confining stratum only 10 or 20 ft thick may provide a satisfactory seal to retain oil and gas. However, the risk would be too great to use beds of this thickness to confine industrial wastes because the formation would be very susceptible to fracturing during waste injection and also could contain thin natural fractures as shown in Figure 6.

Sedimentary rocks originally were deposited in uniform layers at the bottom of ancient seas; however, some were later uplifted, folded, and faulted by forces in the earth's crust into anticlinal (positive) and synclinal (negative) structures as shown by Figure 7. Oil and gas often occur in anticlinal folds because they are less dense than water and seek a position of lowest fluid potential. Hence, it is probable that injected waste with a density less than that of interstitial water would tend to remain trapped in a closed anticlinal structure (Fig. 7A), whereas waste with a density greater than interstitial water would tend to remain in a closed synclinal structure (Fig. 7B).

Faults, defined by Lahee (12) as a failure along which there has been slippage of the contiguous masses against each other, offset strata and place them in contact with other older or younger beds of the same or different rock types, as shown in Figure 8. Fractured formations should not be considered for confining or disposal of wastes.

Other geologic configurations suitable for the confinement of limited volumes of liquid waste, depending on their areal extent, are sandstone lenses with both vertical and horizontal confining beds (Fig. 9) and stratigraphic traps (Fig. 10).

In addition to stratigraphy, structure, and rock properties, aquifer hydrodynamics may be significant in the evaluation of waste-injection well sites. The presence of a natural hydro-dynamic gradient in the injection zone will cause the injected waste to be distributed asymmetrically around the wellbore and transported through the aquifer even after injection has ceased. Several aspects of the subsurface movement of natural fluids or injected wastes under a hydrodynamic gradient are discussed by Young and Galley (15).

FIGURE 6 :Fluid Migrating Upward
        Through a Fractured Confining
        Formation.
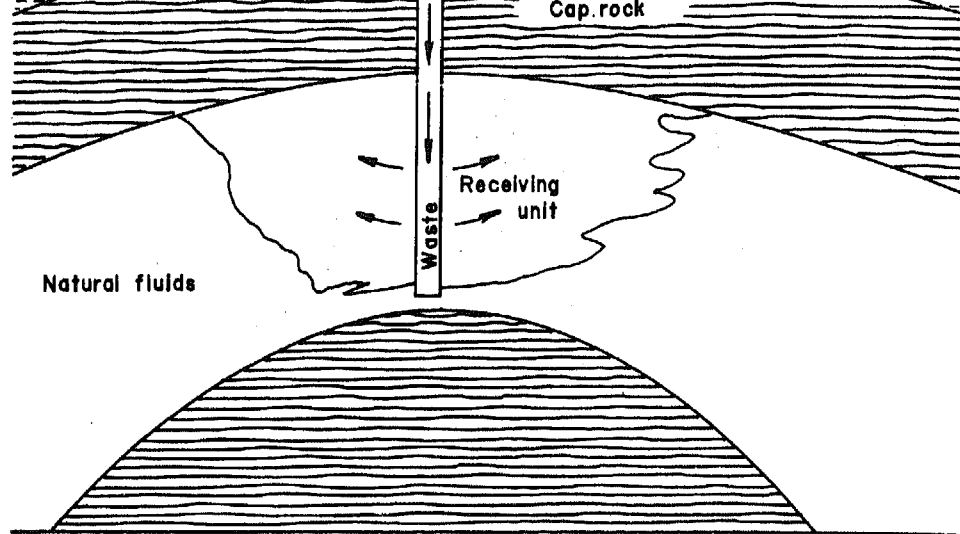
A.–Anticlinal structure with injected liquid waste less dense than interstitial water.
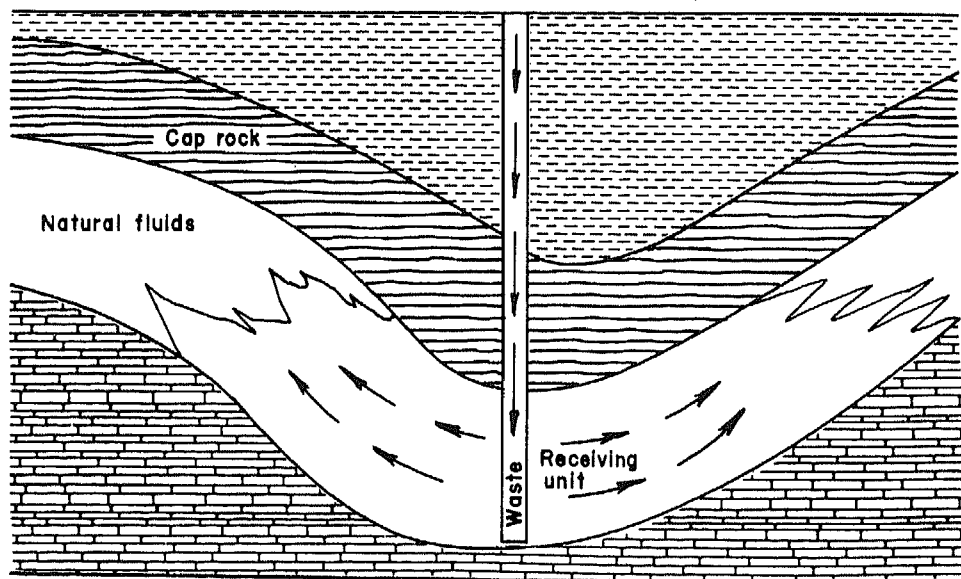
B.–Synclinal structure with injected liquid waste denser than interstitial water.

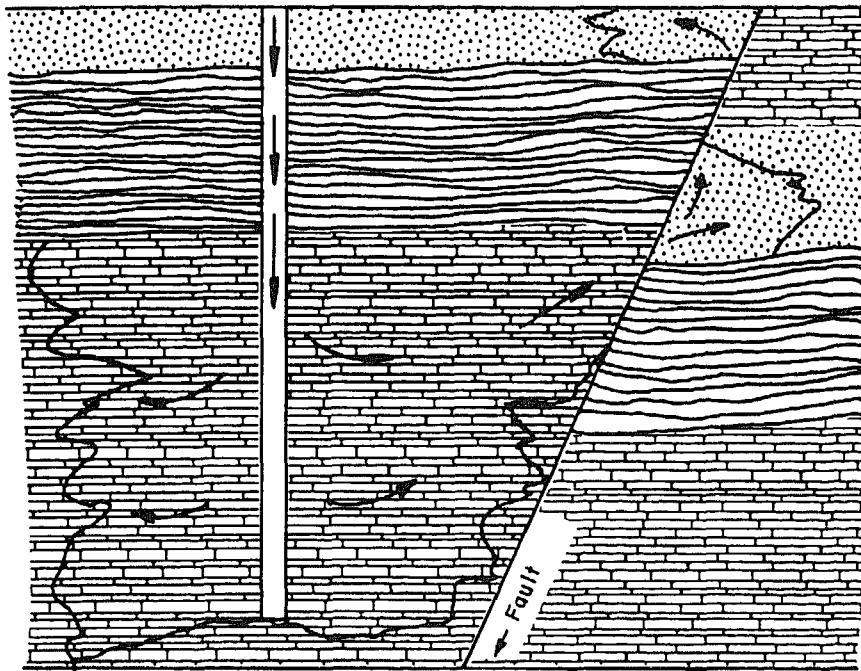FIGURE 7 .– Configurations From Folded Sedimentary Rocks.

FIGURE 8 .-Faulted Formation Showing How Injected
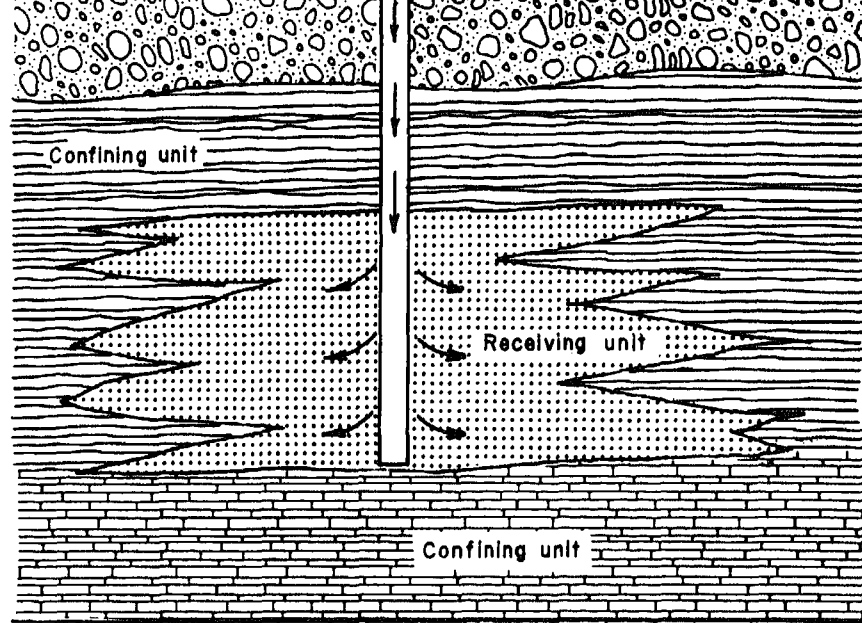Fluid Could be Lost to Another Formation.

FIGURE 9 .- Sandstone Lens With Horizontal and
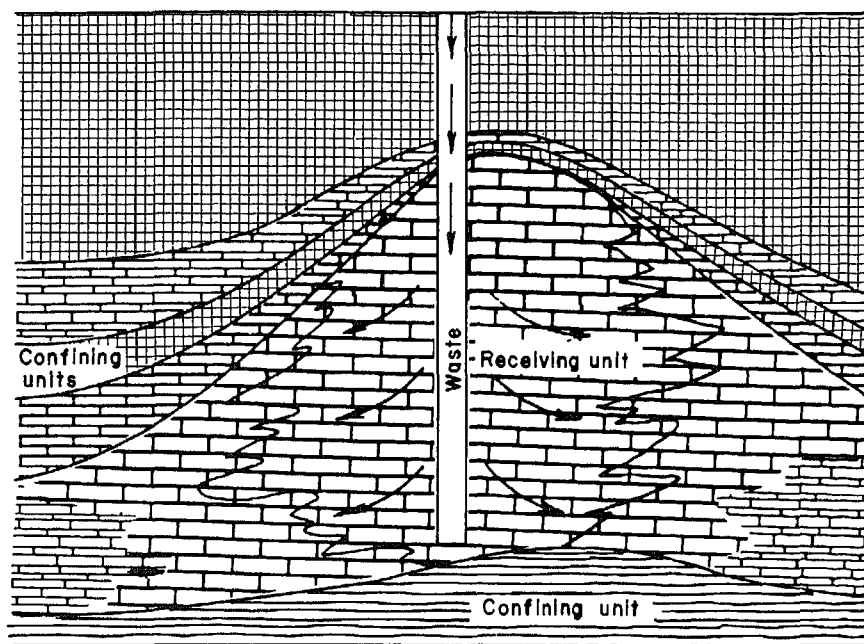Vertical Confining Formations.

FIGURE 10 .— Stratigraphic Trap

posal system will depend on the amount of space that can be made available for waste storage by compression of the interstitial fluids (gas and brine) and the rock matrix. The reservoir pressure will gradually build to a point where continued injection would be inadvisable because of possible fracturing of the confining strata. However, of the disposal installations that were studied in detail (6), no limitations of fluid injection were experienced as a result of excessive pressure caused by fluid confinement.

Sandstone, vugular carbonate (limestone and dolomite) formations, and unconsolidated sand are the three general lithologic types that are currently being used for injection of industrial wastes.

The permeability and porosity of unconsolidated sand units cannot be determined accurately in a laboratory. These properties vary with the degree and method of compaction, and it is impossible to duplicate the subsurface conditions in a small laboratory sample.

Some consolidated sandstone formations are quite homogeneous over wide areas; thus, laboratory analyses of permeability and porosity of cores taken throughout the thickness of the formation are very useful in well completion and analysis of problems that develop later in the life of the well. The Mount Simon Formation near Gary, Indiana, is being used for injection of waste steel-pickling acids, such as Wastes 16 and 17 of Table 2. The average porosity of 14.7% and permeability of 456 md are fairly consistent throughout the range in depth.

Vugular carbonate formations are difficult to evaluate in the laboratory because the vugs are so diverse in size and shape, ranging from microscopic pinholes to vugs the diameter of a pencil. The best method of evaluation is through pumping tests after well completion.

HISTORY OF AN INJECTION SYSTEM

Source and Nature of the Waste: When the plant was put into operation in 1962, two large holding ponds were constructed in an attempt to contain and evaporate the waste generated in the plant. One of these ponds was unsuccessfully used as an algae stabilization pond in an attempt to control the BOD such that the waste might be disposed of into a nearby river. Because of lack of significant solar evaporation in the area, these ponds remained

that were under rice cultivation.

Prior to 1965, the manufacturing facilities were confined to the production of acetaldehyde, butanol, and other organic compounds by cracking natural gas. The waste from these operations consisted of cooling-tower and boiler-water waste containing about 1.1 wt% organic compounds (Table 4). This waste is injected into Well 1, which was completed in July 1964, at a rate between 417,000 and 576,000 gal/day.

In 1965, the plant was expanded, particularly the acetaldehyde program, and hexamethylenediamine and vinyl acetate are additional products that were included during expansion of the plant. The volume of waste from the new units (Table 5) varies from 36,000 to 280,000 gal/day. Since April 1965, this waste has been injected into a second well located 1,200 ft from the first well (9).

Geology: The wells are located near the Gulf Coast of Texas. The area is characterized by the outcrop of the Beaumont Clay. Recent alluvial deposits border the Colorado River and some of its tributaries. Immediately underlying the Beaumont Clay is the Lissie Formation, which extends to a depth of approximately 1,300 ft. These Pleistocene rocks consist predominately of sand and sandstone with intercalated shale and clay and overlie an undetermined thickness (greater than 11,000 ft) of largely undifferentiated sand, sandstone, and shale of Tertiary age. These Gulf Coast formations strike generally east-northeast and dip toward the southeast at approximately 30 ft/mile.

The interval chosen to receive the fluid waste is a well-developed persistent thick sand bed of considerable areal extent. It occurs at a depth of approximately 3,400 ft and is about 250 ft thick over several miles. Electric logs of oil exploration tests in the area indicate it to be predominantly well-sorted, fine-grained sand containing highly saline water. The interval is not productive of hydrocarbons in the region, the shallowest oil and gas production in the area being from the Frio sand at approximately 10,000 ft.

Surface Equipment: The two waste streams are treated separately, but in a similar manner. The waste from the various processes is accumulated in the process waste sump, which is a cement pit constructed low enough in the ground to take advantage of gravity drainage from the units. The composite waste is pumped from the sump to a settler-skimmer where oil and sediments are removed.

Organic constituents, ppm:	
Acetaldehyde	1,000
Acetaldol	900
Acetic acid	5,000
Butanol-1	1,300
Butyraldehyde	1,100
Chloroacetaldehyde	800
Crotonaldehyde	400
Phenol	1,200
Propionic acid	2,200
Inorganic constituents, ppm:	
Calcium	100
Iron	10
Magnesium	50
Sodium	3,000
Chloride	2,000
Sulfate	100
General Properties:	
Total hardness ppm	350
Conductance micromhos	10,000
pH	5
Temperature ° F	160

TABLE 5. - Composition of waste injected into well 2,

(Color: pale yellow, cloudy; odor: stale fish)

| Organic constituents, ppm:	
Ammonia	500
Amyl alcohol	600
Cyclohexane	200
Dodecane	100
Hexanol	1,000
1-Hexylamine	1,400
1,2-Hexylamine	300
Methanol	200
Valeric acid	900
Inorganic constituents, ppm:	
Ammonium nitrate	4,000
Sodium bicarbonate	3,000
Sodium carbonate	600
Sodium nitrate	6,000
Sodium nitrite	7,000
Copper	80
Vanadium	20
Manganese	50
General properties:	
pH	9
Temperature ° F	120
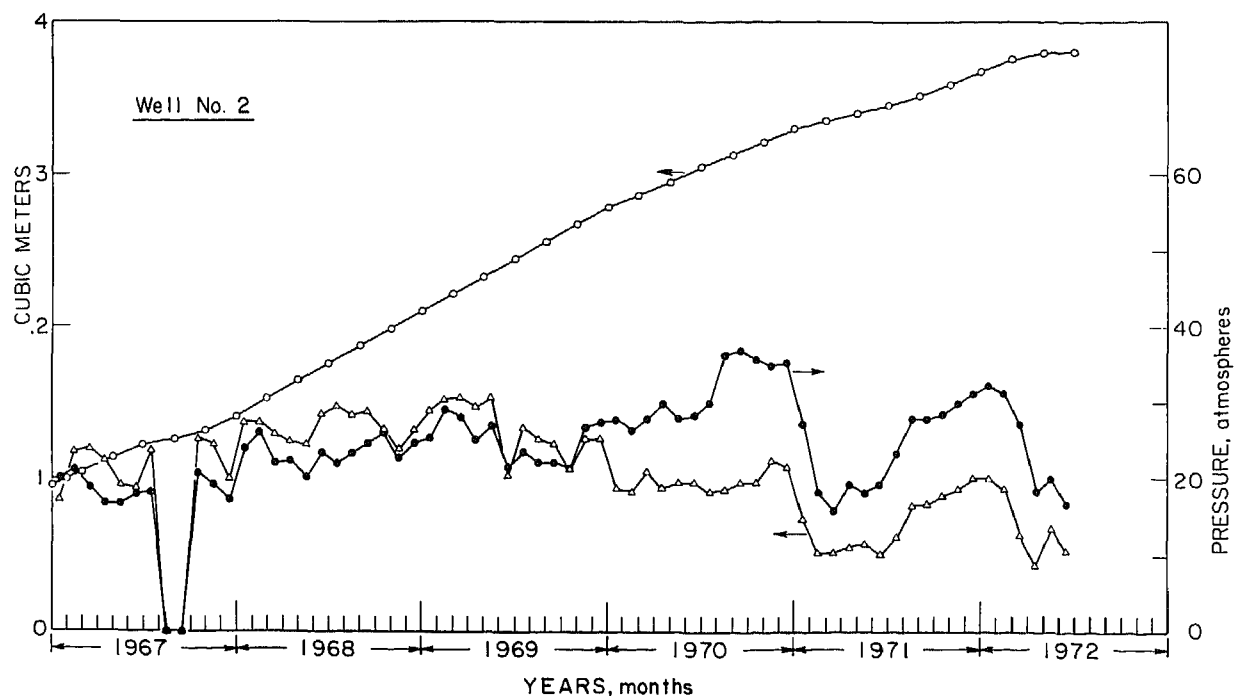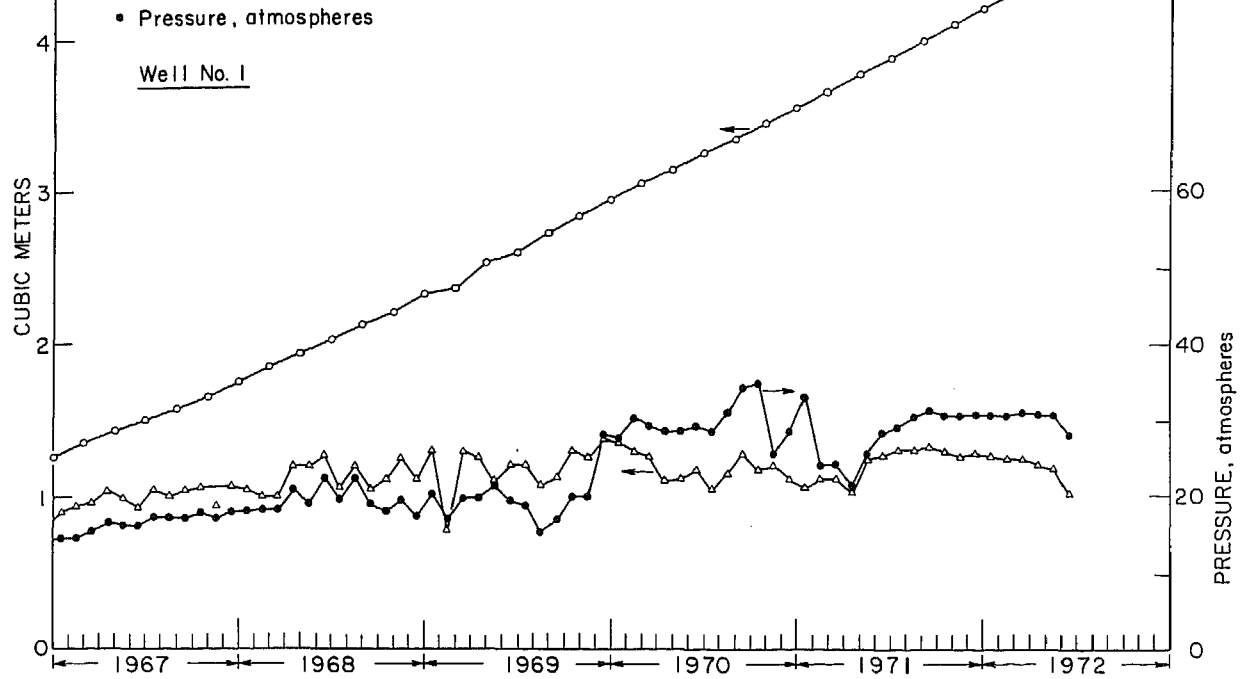
FIGURE 11. - Operating Histories of
Two Injection Wells.

a tarlike mass. After pH adjustment, the waste undergoes filtration in two stages: (1) removal of the major portion of the suspended solids with a leaf filter using diatomaceous earth precoat, and (2) final filtration with cartridge-type high-pressure filters.

Two centrifugal pumps are used as needed to inject the waste from a surge tank into Well 1. Waste 2 is pumped from the setter-skimmer through two cartridge-type filters to a surge tank. Two centrifugal pumps are used as needed to inject the waste into Well 2.

Well Completion and Operation: The surface casing of the first well consists of 10 3/4-in J-55 pipe set at a depth of 1,500 ft and cemented to the surface to protect freshwater bearing sands. A string of 7-in J-55 casing is set from the surface to the bottom of the well at 3,750 ft and cemented in with a special acid-resistant cement. The injection string is 4 1/2-in fiberglass tubing that is also cemented with the special acid-resistant cement. When this tubing was installed, the joints were made up with epoxy resin to insure a good seal. Perforations were made through both casings from 3,400 to 3,600 ft. Injection was started in November 1964.

Well 2 is 2,750 ft from Well 1. The surface string in Well 2 is 13 3/8-in H-40 casing set at 1,400 ft and cemented to the surface to protect the freshwater-bearing sands. A string of 9 5/8-in J-55 casing is set from the surface to the bottom of the hole at 3,750 ft and cemented in place. This casing is perforated from 3,500 to 3,600 ft. Injection into this well was started in April 1965.

Figures 11A and 11B show the well injection histories of Wells 1 and 2, respectively. The average monthly volumes injected and wellhead pressures remained in synchronization with no abnormalities until November 1969, when an obvious increase in the wellhead pressure of both wells occurred. This is undoubtedly due to mutual interference between the wells that began in November 1969 and became progressively more pronounced as injection of fluid continued.

CONCLUSIONS

It is apparent that injection of liquid wastes into deep geologic formations can solve many difficult waste-disposal problems. However, limitations of the knowledge of how the waste

hazards of underground waste injection should receive careful consideration in the planning stages.

The chemical and physical interactions of the waste constituents with the geologic materials at the temperatures and pressures that prevail in the subsurface environment are unknown. However, there is some evidence to indicate that adsorption and chemical reaction will retard the advance of waste constituents away from the well bore. Instead of complete volumetric displacement, the waste constituents are probably stratified behind an advancing liquid front of water containing dissolved salts not too dissimilar from the native formation brine. Accurate predictions of the migration patterns of waste constituents cannot be made until the adsorption, chemical reaction, and ion-exchange properties of each component of the waste mixture are known.

An accurate estimate of the total cost of a proposed waste-injection system can be made only when complete analyses of the waste, geologic formation, and native brine are available. A thorough evaluation of the waste must be made with respect to suspended solids, ranges of pH that promote precipitation, and chemical compatibility with the underground brine. The formation must be studied to determine the porosity, permeability, thickness, areal extent, lithology, and pore-size distribution. When these analyses are obtained, the design and cost estimate of the surface equipment and injection well can be made.

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Chairman: Ralph Scott

Co-Chairman: G. L. Wiesenfeld

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Data on the treatment of aqueous coal conversion waste are needed to ensure that water supply and quality are not adversely affected by the developing coal conversion industry. This work is not intended to develop new wastewater treatment processes, but to provide useful and timely information on the application of known control technologies to coal conversion wastewaters.

Samples of lignitic coal and steam-plant fly ash have been tested for their ability to remove polyaromatic hydrocarbons (PAHs) and refractory phenolics from aqueous streams. Removal of up to 99% of the organics was obtained with solid loadings as high as 15 mg/g. In experiments with a tapered fluidized-bed bioreactor, phenol reductions of $\sim$ 99.9% were achieved at phenol degradation rates of 7 to 10 kg per day per m^3 of reactor volume. Ozonation tests have shown that, with biologically treated wastewater, 99% of the residual phenol and 22 to 97% of the refractory PAHs, along with most of the associated colors and odors, can be degraded using ozone dosages of 0.01 to 0.14 kg per thousand liters. Experiments using wet oxidation for the destruction of both soluble and absorbed organics have been initiated. (Research sponsored by the Division of Environmental Control Technology, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.)

CONTROL ASPECTS OF UNDERGROUND COAL GASIFICATION
a. Preliminary Environmental Results of the LETC Hanna III
Underground Coal Gasification Experiment
Joseph E. Virgona, Theodore C. Bartke, and John E. Boysen
U.S. Department of Energy
Laramie Energy Technology Center

b. LLL Investigations of Ground-Water and Subsidence Effects*.
S. Warren Mead, Francis T. Wang, and Harold C. Ganow
Lawrence Livermore Laboratory

Changes in ground-water quality and the possible effects of subsidence and ground movement induced by the underground gasification cavity represent significant environmental concerns associated with undergroundccoal gasification (UCG). Parallel environmental studies are being conducted by the Laramie Energy Technology Center (LETC) and the Lawrence Livermore Laboratory (LLL) near Hanna and Gillette, Wyoming, respectively, to characterize these

termined.

Their first paper (Part I) discusses the LETC Hanna III environmental studies. The Hanna III experiment (June–July, 1977) was designed primarily to provide information on the potential impacts of UCG on ground-water quality and the environmental control technology implications of those impacts. In addition, parameters critical to the process itself were examined. Preliminary results of the ground-water monitoring during the pre-operational, operational, and early portion of the post-operational phases will be presented.

The second paper (Part II) covers ground-water and subsidence measurements carried out at the sites of two in situ coal gasification experiments conducted in northeastern Wyoming by LLL. Ground-water measurements and complementary laboratory studies have helped to clarify the environmental significance of reaction-product contaminants that remain underground following gasification. Extensive roof collapse into the gasification cavity has been documented by subsurface geotechnical measurements.

ANALYTICAL STUDY OF THE EFFLUENTS FROM A HIGH-TEMPERATURE ENTRAINED FLOW COAL GASIFIER

L. D. Hansen, L. R. Phillips, R. B. Ahlgren, N. F. Mangelson, D. J. Eatough, and M. L. Lee

Bringham Young University

Effluent streams from a 100 pound per hour, pressurized, high temperature, entrained flow coal gasifier have been found to be extremely clean compared to those of other gasifiers. The water-scrubbed gaseous effluent contained only CO, H_2, CO_2, N_2, CH_4, and traces of H_2S and HCN. The gas obtained by depressurization of the scrubber water contained trace amounts of SO_2 in addition to these other seven gases. Polycyclic aromatic hydrocarbons, the only non-volatile organic compounds found in the scrubber water,

and inorganic species were found to be below the level of environmental concerns. Statistical analysis was used to determine the effects of the process parameters: coal type, coal feed rate, reactor pressure, oxygen to coal ration, and stream to coal ratio.

Sufficient environmental control can be achieved by removing the H_2S from the gaseous effluent using an appropriate commercial process and by separating the particulate matter from the scrubber water. Particulate matter separation methods include floculation settling, froth flotation and filtration. Floculation is probably the most economical of these separation methods. Laboratory bench scale separation tests and mass balance calculations should provide valuable information as to which environmental control technology is most economically feasible.

CLEANING PRODUCER GAS FROM THE METC GASIFIER

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U.S. Department of Energy
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ABSTRACT

The Morgantown Energy Technology Center (METC) of the Department of Energy is developing a system to clean Low-Btu gas made from coal. The gas is generated in a prototype pressurized stirred fixed-bed gas producer developed in earlier work at METC that gasifies 909 Kg/hr (1 tph) of caking bituminous coal. The objective is to clean the gas to the degree needed both by any end-use system consuming the gas, and to ensure that effluents from the end-use system meet emission requirement. This report described pilot-scale development of a prototype gas cleanup system using a sidestream protion of the full 4,248,000 lit/hr (150,000 scfh) gas output from the METC gas producer. A full-flow gas cleanup system, developed as a result of the sidestream pilot-scale test investigations, is being installed and tested in phases throughout 1978. Experience with particulate, tar, light oil, and alkali removal with the side stream scrubber and experience with particulate and tar removal in the developmental testing of the full stream scrubber are reviewed.

Quench water is a principal wastewater from coal conversion processes that employ wet cleaning of gasses. The origin of the water is moisture in the coal and steam injected into the coal conversion reactor. Depending upon coal composition the quench water contains chlorides, flourides, ammonia, hydrogen sulfide and sulfur oxides. With tar producing coal conversion technology the quench water also contains cyanides, thiocyanates, phenols and various organics.

A two stage gas quenching process was proposed to absorb strong electrolytes in a small flow first-stage quench so as to improve the feasibility of reuse of the larger volume second-stage quench. A study was made to compare the technical and economic feasibility of two-stage quenching with conventional single-stage quenching.

The study evaluated methodology for estimation of quench water characteristics and engineered a concept for accomplishment of the two-stage quench. The results indicated that strong electrolytes could be absorbed from the gasses to a high degree in a first-stage quench with a blowdown of from 5 to 10 percent of the total condensate. The blowdown would be purged to waste disposal. The second-stage quench would collect 90-95 percent of the condensate containing a low content of strong electrolytes. The condensate containing weak electrolytes and organics would be treated by steam stripping and bioxidation prior to reuse as process water. Alternative disposal concepts were evaluated for two sites using representative Eastern and Western coals.

ENVIRONMENTAL CONTROL ACTIVITIES ON
SLAGGING FIXED-BED GASIFICATION AT THE
GRAND FORKS ENERGY TECHNOLOGY CENTER

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The 25-TPD pilot SFBG at the GFETC was reactivated in 1976 for the purpose of supporting the development and commercialization of the slagging fixed-bed gasification process. A major objective was the development of a detailed environmental assessment, including characterization of both gaseous and liquid effluents. This assessment will substantially apply both to the Hi-Btu demonstration plant currently being designed based on SFBG technology and to fixed-bed, dry-ash Lurgi gasifiers planned for first generation SNG plants.

approach required to meet industrial and regulatory needs; 2) development and application of sampling procedures and analytical methods for characterizing gaseous and liquid effluents; 3) studies on gas cooling, separation of tar and byproducts, and treatment of waste water; 4) studies on disposal of gasifier slag and other waste solids; 5) the relation of effluent properties to gasifier operating variables, and 6) assessment of biomedical effects due to tars and waste water constituents. This report will present a summary of the assessment plan and selected data on the characterization of gaseous and liquid effluents performed to date.

OVERVIEW OF THE SYNTHANE PILOT PLANT
ENVIRONMENTAL ASSURANCE PROGRAM

by

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An historical account of the development and current studies of environmental monitoring and compliance at the SYNTHANE pilot plant will be presented. This account will include the experiences and problems in establishing monitoring programs in the following areas:

Air: Noise:
    Ambient Monitoring   Background
    Stack Testing   In Plant
    Fugitive Emissions

Water: Solid Waste:
    Surface Water Control   Characterization
    NPDES Sampling   Disposal
    Continuous Water Monitoring

Occupation Health:
    Problem and Direction

In February and March 1975 the first ambient air background studies were undertaken at the SYNTHANE pilot plant. Subsequent to these initial studies an environmental monitoring and compliance program was developed incorporating the areas noted above. The cost of this program to date plus facilities and equipment amount to approximately three (3) million dollars. The experience provided in interfacing with the technology development and developing the environmental monitoring and compliance program can be of value to all who are involved in small scale and large scale development.

Data on the treatment of aqueous coal conversion waste are needed to ensure that water supply and quality are not adversely affected by the developing coal conversion industry. This work is not intended to develop new wastewater treatment processes but to provide useful and timely information on the application of known control technologies to coal conversion wastewaters.

Samples of lignitic coal and steam-plant fly ash have been tested for their ability to remove polynuclear aromatic hydrocarbons (PAHs) and refractory phenolics from aqueous streams. Removal of up to 99% of the organics was obtained. In experiments with a tapered fluidized-bed bioreactor, phenol reductions of $\sim$99.9% were achieved at phenol degradation rates of 7 to 10 kg per day per m^3 of reactor volume. Ozonation tests have shown that, with biologically treated wastewater, 99% of the residual phenol and 22 to 97% of the refractory PAHs, along with most of the associated colors and odors, can be degraded using ozone dosages of <0.25 kg per thousand liters.

1. INTRODUCTION

The abundance of this country's coal resources, relative to those for crude oil and natural gas, has prompted both the Federal government and industry to undertake an intensive effort to develop processes for converting this solid form of energy into substitute gaseous and liquid fuels. Water is an essential raw material for these coal conversion processes. Process cooling is only one of the many reasons for this dependency. Often more than 30% of the energy in the coal feed is discarded as water vapor in the cooling towers. The impurities in the makeup water are discarded as wet sludges and/or blowdown streams heavily laden with contaminants. Water is also used as a source of the hydrogen needed to raise the atomic hydrogen-to-carbon ratio of coal from <1.0 to the approximate 1.5 to 3.5 values found in crude oil and natural gas, respectively. Depending on the hydrogen production process,

It has been estimated that by the year 2000 wastewater discharges from all types of coal conversion facilities will total nearly 700 million tons/year.[1]

Environmental and economic reasons will compel developers of coal conversion processes to maximize water reuse and to reduce pollutant levels in aqueous effluents. Because of the economic incentives favoring location of a coal conversion facility close to the mine mouth, water resources available to such a plant will be either relatively scarce and highly competed for by nonindustrial users such as farmers, municipalities, and recreationists (as in Colorado, Wyoming, Montana, North Dakota, and New Mexico), or they will be relatively abundant but heavily used by other industrial facilities (as in Kentucky, West Virginia, and Illinois). Environmental considerations aside, recovery of dissolved "pollutants" as process by-products (e.g., phenol) may become economically desirable because of raw material scarcities; however, it is difficult to justify at the present time, except for very large-scale conversion plants. Thus, ensuring the availability of adequate technology for treating the wastewaters from coal conversion processes may be as necessary a part of fostering the commercialization of a synthetic fuels industry as the development of the coal conversion technology itself.

Only recently has the development of the necessary control technology for the cleanup of coal wastewaters gained sufficient emphasis to consider its integration into the coal conversion implementation program. However, most control technology studies are considered to be add-ons for a particular coal conversion process. Unfortunately this viewpoint is often encouraged by the separation of those charged with the development of the technology from those investigating the technology available for the cleanup of aqueous streams. In many cases, judicious design of the various individual conversion process modules could allow minimal control modifications to clean up much of the wastewater problem. Given that the discharge of a wastewater stream is unavoidable, the determination of the amount of cleanup needed is a function of both present and future effluent regulations and of the proposed use of the effluent water. The development of these future regulations is presently causing a good deal of concern to those within EPA and to other investigators in the field.

2. COMPOSITION OF COAL CONVERSION WASTEWATER

Recent studies[2-5] of several coal gasification and liquefaction processes have identified the following operations as sources of wastewater: (1) separation of excess water from raw liquid products, (2) quenching and scrubbing of raw fuel gas, and (3) desulfurization and demetallization of raw liquid products. Other parts of the overall processes will provide additional sources of wastewater: (1) coal storage

Although wide variations exist in the composition of coal conversion wastewaters, generalizations can be formulated, depending on the type of process, operating conditions, and the nature of the coal used. The major constituents and concentrations of a representative wastewater are listed in Table 1.[2] The high phenol and ammonia concentrations are typical of coal conversion process wastewaters, whether they are condensation liquors or scrubber waters. Also listed are the concentration ranges expected in future Federal regulations for a variety of components. Standards for related industries such as coking and petroleum refining were used to develop these values[2,6-7] because there are as yet no regulations for the coal conversion industry. As shown, the levels of all the components listed will far exceed the limits of the anticipated regulations.

Individual variations do exist between the component concentrations of the various wastewaters. Although these variations are not shown, they may be quite important in the consideration of specific control technologies. The presence of a significant quantity of a metallic compound, for example, could alter the effectiveness of a biological or oxidative treatment system.

A survey of the literature reveals a number of presently available and proposed technologies for the cleanup of wastewaters with compositions similar to those indicated in Table 1.[2] As expected, they represent a wide range of removal efficiencies, final residual concentration levels, and costs. Efforts to obtain the relative economic costs of various environmental control technologies for the treatment of aqueous wastes from coal conversion processes have been completed.[2] Six processes have been identified as potentially promising in this area: ozonation, adsorption, biological degradation, solvent extraction, membrane processes, and coagulation-flocculation. The economic position of the various control technologies is shown in Fig. 1 where treatment costs are plotted versus residual organic levels.

3. ORNL'S WASTEWATER TREATMENT PROGRAM

ORNL's involvement in environmental control technology consists of an assessment and screening test evaluation of the amenability of coal hydrocarbonization wastewater and other coal conversion wastewaters to various treatment technologies. As part of this program, a flow sheet was proposed that takes advantage of several available unit operations and addresses the complete treatment of coal conversion wastewaters. This processing scheme is shown in Fig. 2 and includes physical, chemical, and biological treatment of the waste stream. The unit operations that are being investigated at ORNL include the bioreactor, the adsorption

Table 1. Composition of a typical coal conversion wastewater

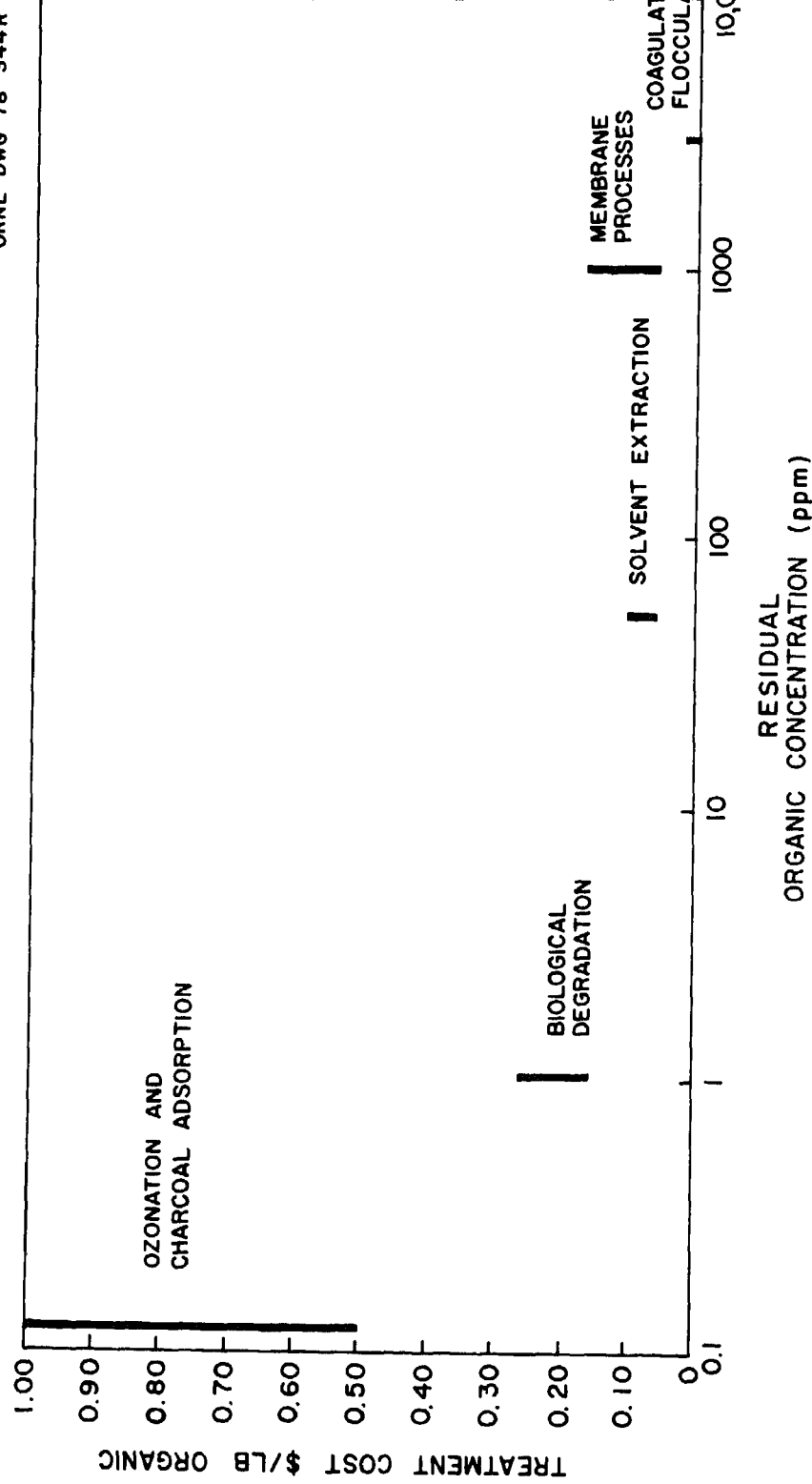| Component	Concentration in wastewater ($\mu g/cm^3$)	Limits of anticipated regulations ($\mu g/cm^3$)	
Phenol	6,000		0.03-0.3
NH_3	10,000		0.8 -5.0
H_2S	1,000		0.02-0.2
CN^-	100		0.02-0.1
SCN^-	500		
PAH	10		
TOC	20,000	BOD	4-30
		COD	20-350

Fig. 1. Economic costs of environmental control
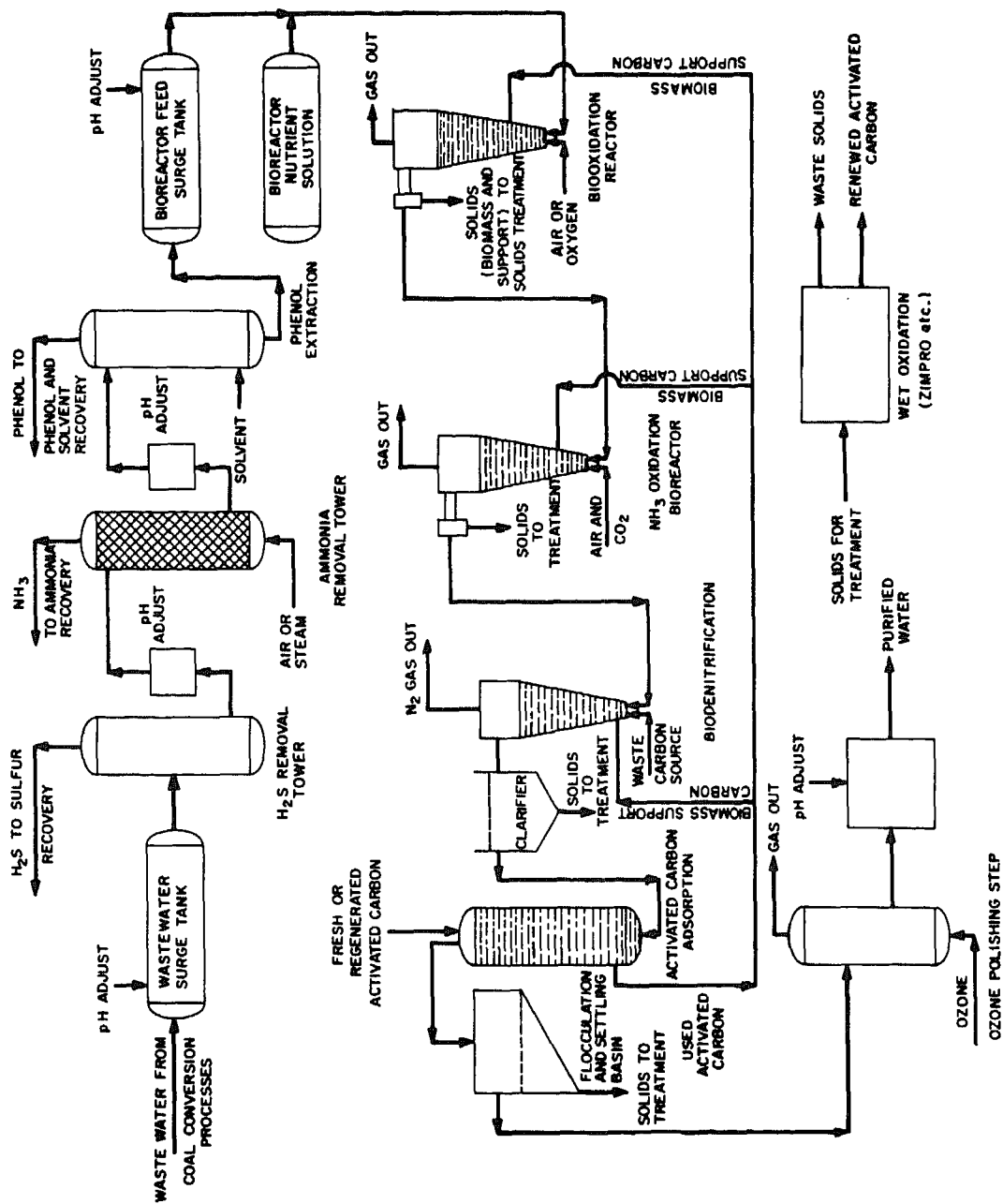technologies for aqueous coal conversion wastes.

Fig. 2. Proposed integrated flow sheet for treatment
of aqueous coal conversion wastes.

The development of this flow sheet is being pursued with a mass balance and economic cost analysis of an integrated control scheme for a commercial-scale, 30,000-ton/day SRC-I coal conversion plant producing $\sim$3000 gal of wastewater per hour.

A tapered fluidized-bed bioreactor that has been adapted to the treatment of coal conversion wastewater is used in the biological step. This tapered fluidized-bed bioreactor system, shown in Fig. 3, consists of a tapered (2.5- to 7.6-cm) section containing a solid support to which bacteria can adhere. The solid support, which is generally a substance such as coal or sand of $\sim$30/60-mesh particle size, is fluidized by the flow of the waste stream to be treated. The tapered bed permits a wide range of fluidizing conditions and allows for expansion of the bed as biomass accumulates on the particles. In addition, the tapered section produces few large eddies and tends to minimize back-mixing when used for two-phase (i.e., liquid-solid) systems.

The chief advantage of the fluidized-bed system is the high concentration of bacteria,[8] which is made possible by the large surface area available on the small particles. Also, particles with excess cells can be easily removed and fresh particles added to the reactor while operation continues. In cases where oxygen is needed for metabolism, the reactor is operated as a three-phase fluidized bed and is sparged with oxygen.

The unit, which has been in operation for more than 1.5 years, has treated the aqueous waste produced by the ORNL Coal Hydrocarbonization Bench-Scale Facility. Some preliminary results indicate that the tapered fluidized-bed bioreactor in a single contacting stage can reduce the phenol and thiocyanate levels in the aqueous waste to ≤ 1 $\mu g/cm^3$ and 1 to 5 $\mu g/cm^3$, respectively, at rates up to 5 to 10 kg of phenol and 1.5 to 1 kg of thiocyanate per m^3 of reactor volume per day at a flow rate of 500 cm^3/min. In the fluidized-bed bioreactor using the hydrocarbonization scrubber water as a reactor feed, and when operated for phenol degradation, the total soluble organic content is reduced an average of 95%, whereas phenol is reduced an average of >99.5%. The concentrations of other organic components (PAHs, xylenols, etc.) are also decreased to some extent, depending on the chemical species involved and the residence time available in the reactor.[9]

As a final polishing step to remove any biologically refractive compounds, ORNL is assessing the feasibility of using adsorptive materials other than expensive activated charcoal. Recent investigations have centered on synthetic resins, fly ash, and several lignitic coals. Although the ash and coals do not have the very high adsorptive capacity of activated charcoal, they generally have relatively high surface areas of $\sim$250 m^2/g, as measured with CO_2.

Both batch sorption tests (isotherm tests) and column screening runs have been performed. In the batch tests, 40 ml of the waste solution and
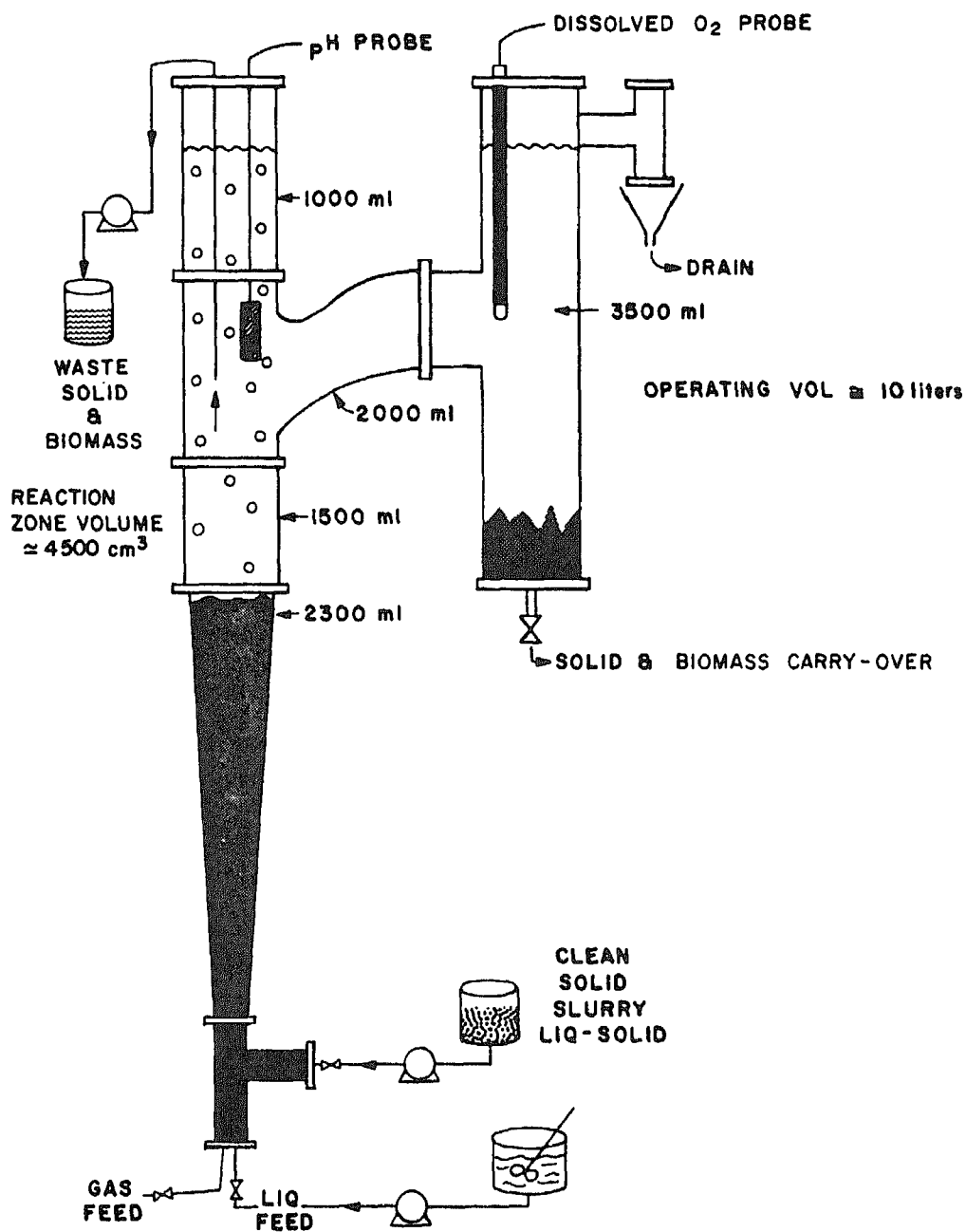
Fig. 3. Schematic drawing of the tapered
fluidized bed bioreactor system.

chloride resin. Some of the adsorption levels may indicate an interest in some of these resins; however, the 4-hr results were not included due to insignificant adsorption.

Column screening tests have recently been performed with two Texas and one North Dakota lignite coals on synthetic wastewater and actual wastewater from the ORNL Coal Hydrocarbonization Facility and a coal tar chemical plant. For the synthetic solutions, both naphthalene and phenanthrene were used as representative, but noncarcinogenic, PAH.

These tests were performed in a packed bed consisting of a 50-ml burette loaded with ~33 g of coal and operated in the upflow mode. The results of one series of tests are shown in Table 3. Because column breakthrough was not reached in most cases, the contaminant loadings reported in Table 3 are minimum values.

Ozonation, an attractive choice for a final cleanup step, is being investigated. In this case, ozonation, normally considered an expensive choice for effluent cleanup, would be used to destroy only those refractory materials that pass through biological treatment. For these screening tests, a small batch ozone reactor was used to treat ORNL biotreated coal hydrocarbonization scrubber water. This system, shown schematically in Fig. 4, consists of a corona discharge ozone generator with a maximum output of 4.5-g/hr, a 1.2-liter reactor, impingers for ozone concentration determination, and a flow-through fluorescence detector. The flow monitor is used to continually follow changes in native fluorescence, which is a gross indicator of the relative abundance of polynuclear aromatic material (PAH). Samples are extracted periodically and analyzed for total organic carbon and phenolic content.

Some preliminary results indicate that ozonation can reduce the phenol and PAH levels in the aqueous wastes to ≤ 0.1 $\mu g/cm^3$ and ≤ 0.25 $\mu g/cm^3$, respectively, with contact times of 15 min or less. In the ozone reactor, the phenol and PAH levels were reduced by 95 to 98%. Optimum operating conditions appear to be 20 to 35°C; pH, 11.2; gas flow, ~0.3 liter/min; and inlet ozone concentration, 70-150 mg ozone per liter of oxygen. Outlet ozone concentration and fraction ozone utilized were not measured. The effects of flow rate, pH, and temperature on rate of fluorescence decrease are shown in Figs. 5 to 7.

4. ONGOING WORK

The objective of our present work is to characterize the effectiveness of the various treatment systems for the cleanup of aqueous coal conversion wastes. Since a number of these concepts are still in the developmental stage, an integrated procedure has been formulated to test

Sorbent	Naphthalene (ppm)		Anthracene (ppm)		Benzanthracene (ppm)		Phenanthrene (ppm)	
	0.3	3.0	0.0375	0.075	0.002	0.01	0.232	1.16
Activated carbon, 1 mg								
4 hr	0.79	0.78	0.73	0.50	0.88	0.90	0.91	0.43
16 hr	0.88	0.96	0.87	0.90	0.94	0.95	0.90	0.77
Resins, 16 hr								
Chelex 100, 1 g	0.69	0.22	--	--	--	--	--	--
IR-120, 1 g	--	0.58	--	--	--	--	0.78	0.93
IRA-400, 1 g	0.83	0.92	--	--	--	--	1.00	1.00
0.1 g	0.40	0.41	1.00	0.97	1.00	0.90	0.97	0.84
AG-MP-50, 1 g	--	--	0.80	0.75	--	--	1.00	0.92
Ash, 1 g, 4 hr								
John Sevier fly ash	--	0.68	--	--	--	--	--	0.93
Kingston fly ash	--	0.78	--	--	--	--	--	0.96
Wyodak hydro-carbonization ash	--	0.59	--	--	--	--	--	0.89

- -

Hydrocarbonization wastewater

Phenol 4.0 (ppm)   Total carbon (107 ppm)

Sorbent	Phenol 4.0 (ppm)	Total carbon (107 ppm)
Texas lignite 1 g, 3 hr	0.20	0.10

Table 3. Adsorption of contaminants from wastewater in a packed column[a]

Sorbent	Solution tested	Concentration (ppm)	Flow rate (mℓ/min)	Coal loading (mg/g coal)	Removal (%)
North Dakota lignite	Naphthalene	3.0	6.0	1.6	
Texas lignite	Naphthalene	3.0	5.0	2.2	95
North Dakota lignite	Phenanthrene	1.16	5.0	1.0	
Texas lignite	Phenanthrene	1.16	1.2	0.4	
Texas lignite	Phenol	200	6.0	2.1	99
Texas lignite	Phenol	50	1.2	1.8	
North Dakota lignite	Coal tar Wastewater	55[b] 1[c]	1.2	0.8[b]	30 60
Amberlite XE-348 carbonaceous resin	Phenol	200	6	112	~99
ORNL hydrocarboni-zation char	Phenol	200	6	~0	~0
Texas Wilcox lignite	Hydrocarboni-zation water	107[d] 4[e]	1.3	1.5[d] 0[e]	8 ~0

[a]All tests run in a standard 50-mℓ burette with ~33 g of sorbent.
[b]Total carbon.
[c]Polynuclear aromatic hydrocarbon.
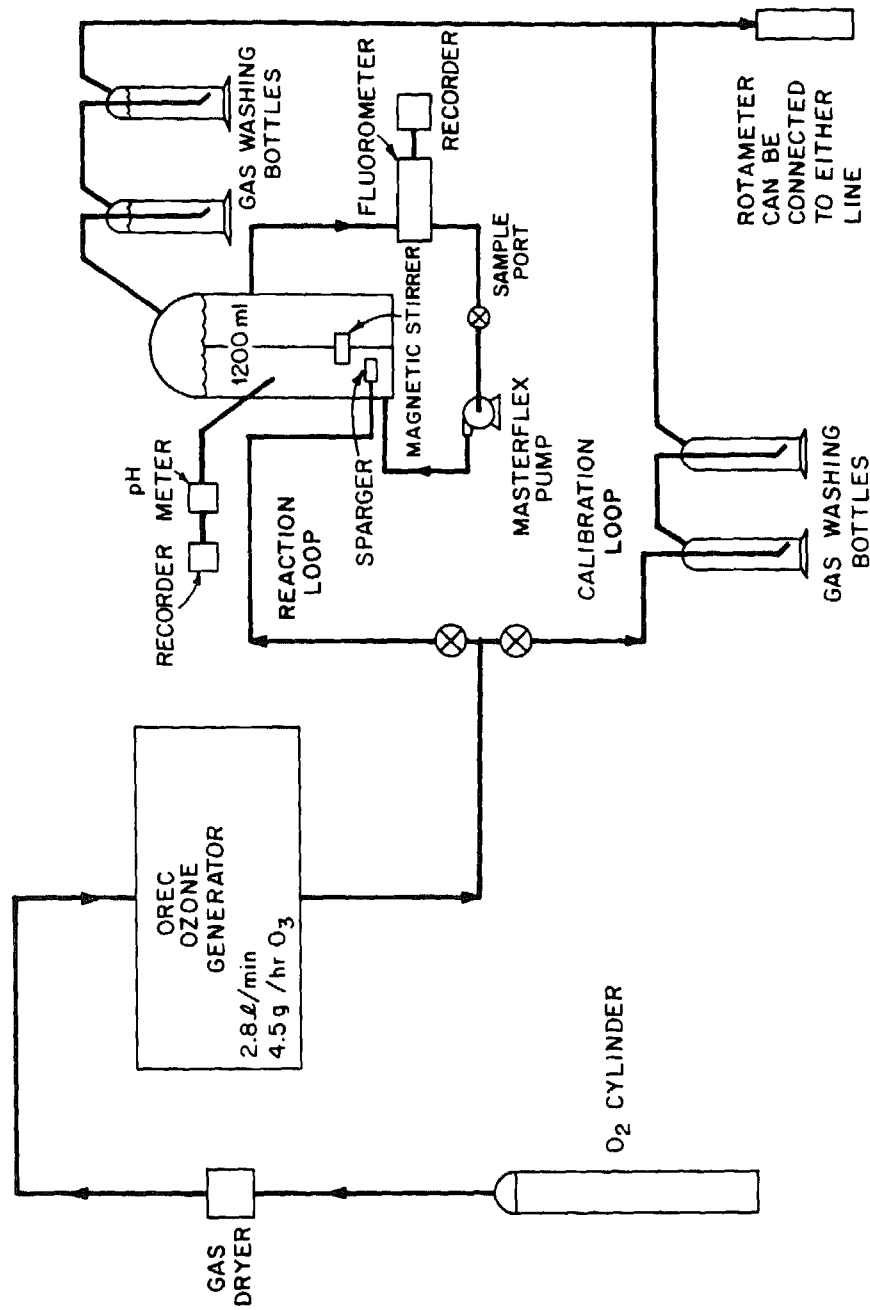[d]Total organic carbon.
[e]Phenol.

Fig. 4. Schematic drawing of batch ozonation system.
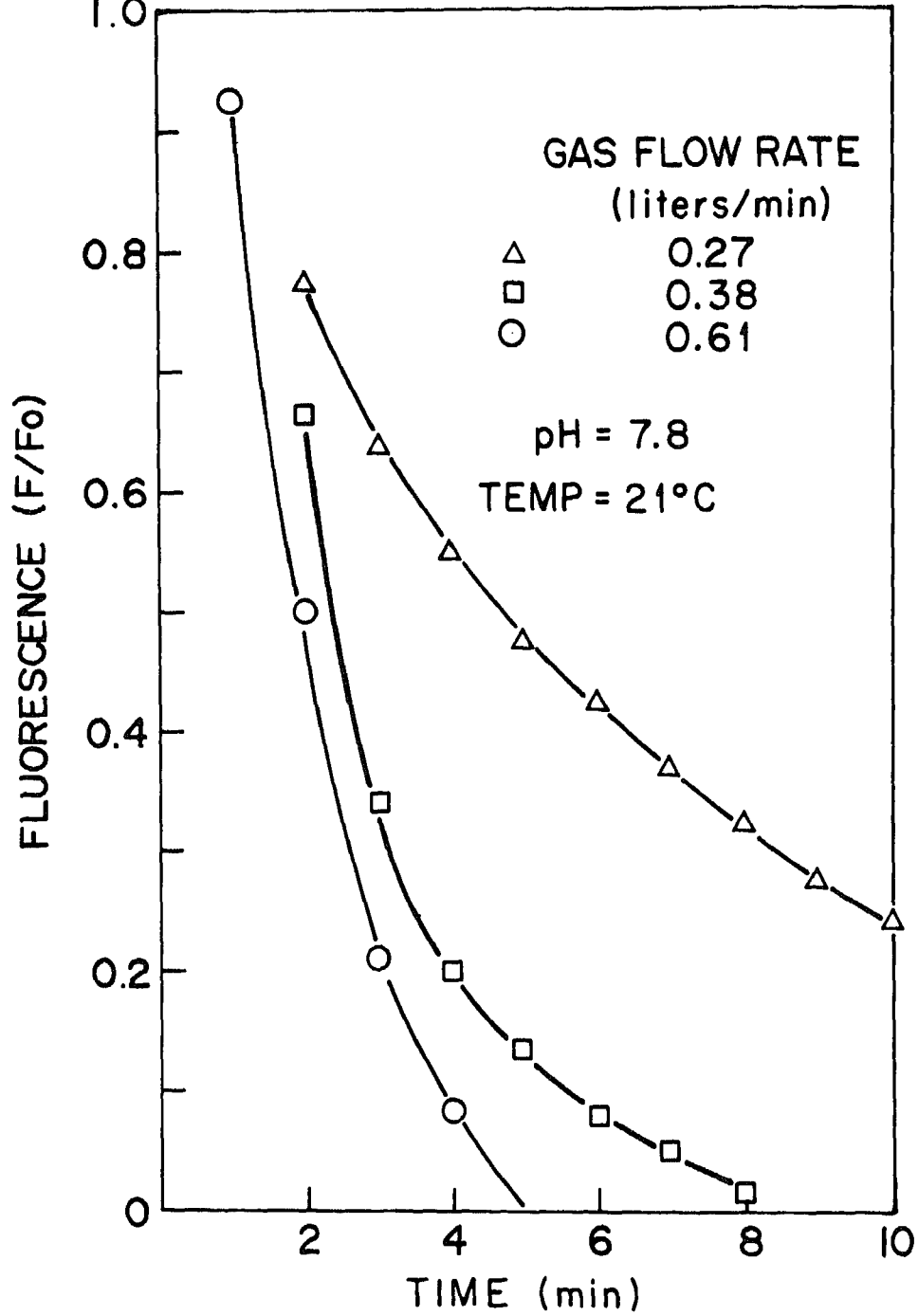
Fig. 5. Ozonation of hydrocarbonization wastewater.
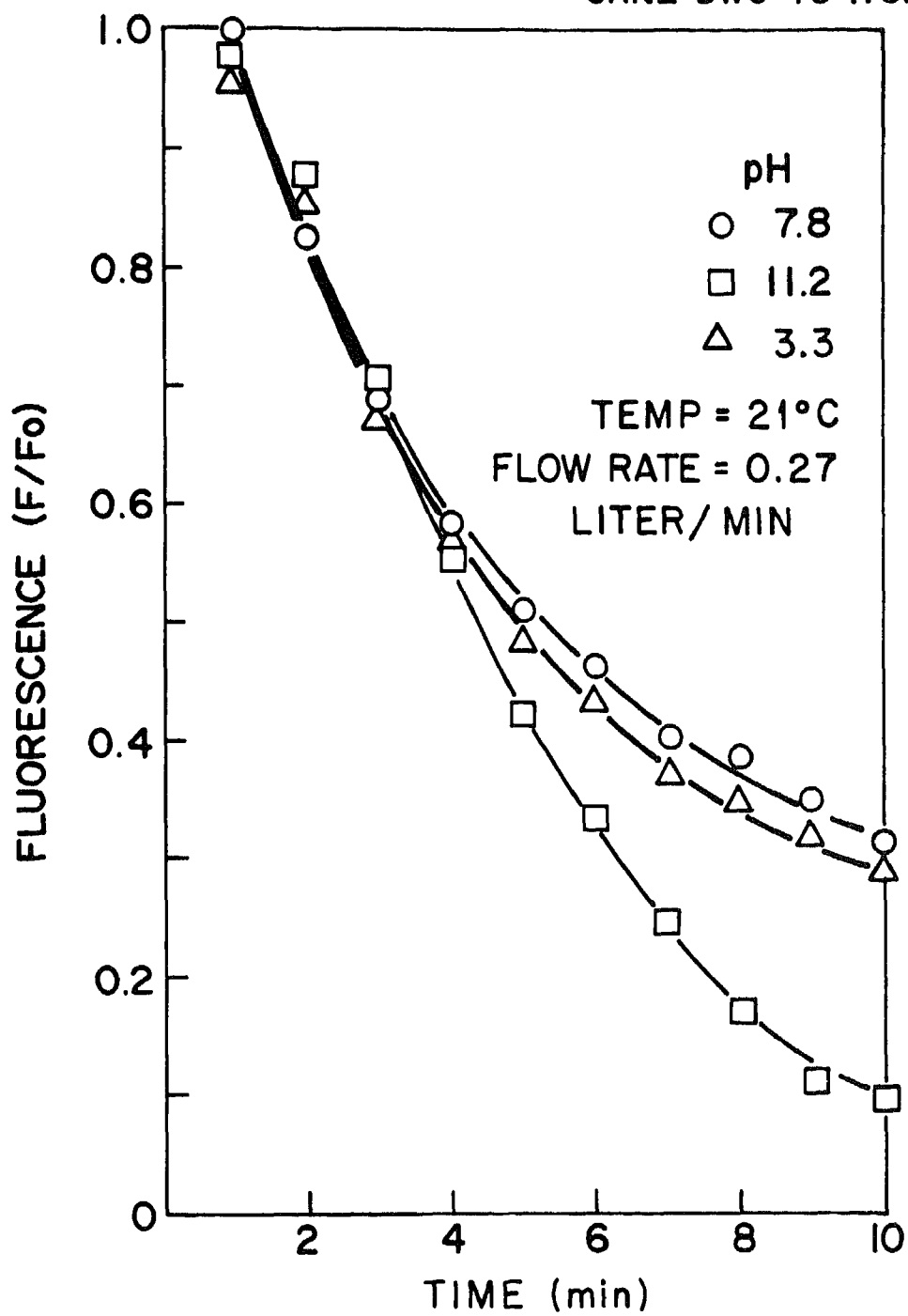Effect of gas flow rate.

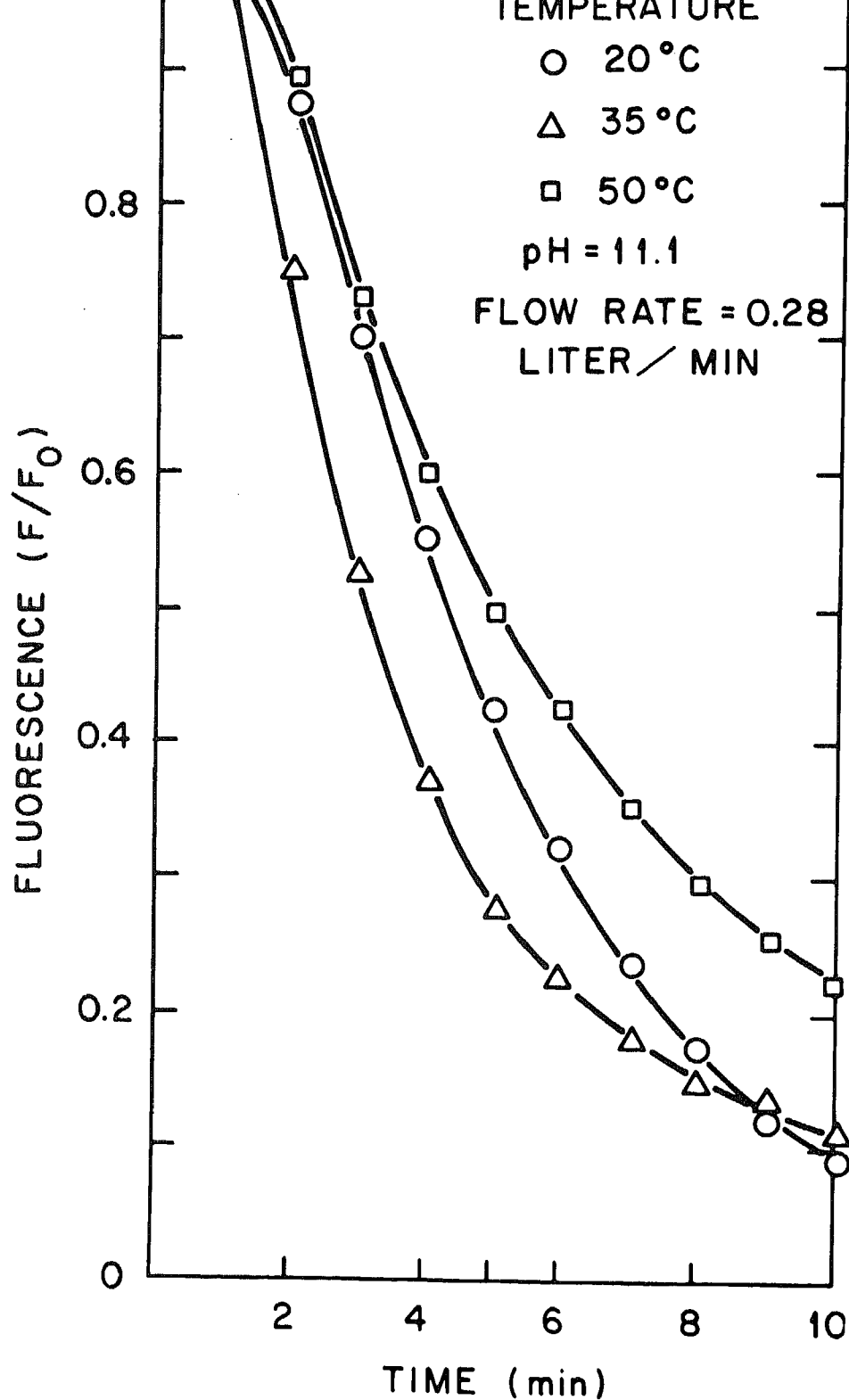Fig. 6. Ozonation of hydrocarbonization wastewater.
Effect of pH.

Fig. 7. Ozonation of hydrocarbonization wastewater.
Effect of temperature.

Technology Divisions of ORNL and is aimed at developing procedures
for characterizing the efficiency of environmental control methods
for any coal conversion effluent. For the initial effort, untreated,
biotreated, and fully treated material from ORNL's hydrocarbonization
experiments will be analyzed, fractionated, and tested for both acute
and mutagenic toxicity.

Future studies will continue to concentrate on removing toxic
organic and carcinogenic compounds. However, additional work will
include integrating the individual cleanup methods into a complete
cleanup system similar to the one shown in Fig. 2.

5. CONCLUSIONS

Although several gasifiers are being developed that are theoreti-
cally capable of being operated under conditions in which they should
produce little, if any, aqueous discharge, most of the developing coal
conversion processes will produce large quantities of effluents. Because
any sour gas cleanup or wet scrubber will transfer pollutants to a water
stream, aqueous discharges will be of great concern and will contain size-
able amounts of known toxic and carcinogenic compounds. Present standards
do not call for specific levels of treatment; however, future standards
will surely be more stringent and will mandate extensive control technology.

The screening of a number of available control technologies has demon-
strated that a combination of control technologies can conceivably be used
to produce an acceptable effluent water stream. To date, however, these
technologies have not been tested on actual wastewater in the field.
Several coal conversion processes are presently being considered for
demonstration-level projects. If indeed the purpose of these projects
is to demonstrate the commercial feasibility of these processes, then it
should also be desirable to demonstrate their environmental acceptability.

Wastewater processing trains incorporating some of both presently
available and advanced techniques should be constructed and used to treat
various coal conversion wastewaters. Although it is not practical to
design these pilot treatment processes to treat all the wastewater from
any of the various demonstration plants, they should provide data on the
treatability of actual wastewater streams and allow evaluations of the
various technologies.

ceedings Environmental Aspects of Fuel Conversion Technology, II, EPA-600/2-76-149, U.S. Environmental Protection Agency, Washington, D.C. (July 1976).

2. J. A. Klein and R. E. Barker, Assessment of Environmental Control Technology for Coal Conversion Aqueous Wastes, ORNL/TM-6263, Oak Ridge National Laboratory, Oak Ridge, Tenn. (July 1978).

3. E. M. Magee, Evaluation of Pollution Control in Fossil Fuel Conversion Processes: Final Report, EPA-650/2-74-009n, U.S. Environmental Protection Agency, Washington, D.C. (January 1976).

4. F. Glaser, A. Hershaft, and R. Shaw, Emissions from Processes Producing Clean Fuels, Applied Research Report BA 9075-015, Booz-Allen, Bethesda, Md. (March 1974).

5. D. B. Emerson, "Liquefaction Environmental Assessment," U. S. Environmental Protection Agency, Washington, D.C., in Symposium Proceedings Environmental Aspects of Fuel Conversion Technology, III, EPA-600/7-78-063 (April 1978).

6. U.S. Environmental Protection Agency, Effluent Guidelines and Standards for Iron and Steel Manufacturing Point Source Category 39FR24114 (June 28, 1974).

7. U.S. Environmental Protection Agency, Effluent Guidelines and Standards for Petroleum Refining Point Source Category 39FR16560 (May 9, 1974); 39FR32614 (Sept. 10, 1974); and 40FR21939 (May 20, 1975).

8. J. S. Jeris et al., "Biological Fluidized-Bed Treatment for BOD and Nitrogen Removal," J. Water Pollut. Control Fed. 49, 816 (1977).

9. J. A. Klein and D. D. Lee, "Biological Treatment of Aqueous Wastes from Coal Conversion Processes," presented at the Symposium on Biotechnology in Energy Production and Conservation, Gatlinburg, Tenn., May 10-12, 1978.

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ABSTRACT

Since 1972 the Laramie Energy Technology Center (LETC) has been seeking
an economically viable process for gasifiying coal underground (1-7). The
LETC has been investigating the potential environmental impacts associated
with underground coal gasification (UCG) at four UCG test sites near Hanna,
Wyoming (8-10). The Hanna III experiment (5-7) was designed to provide
information on the potential impact of UCG on groundwater quality and the
environmental control technology implications of those impacts along with
parameters critical to the process itself. Environmental objectives were:
(1) to characterize the pertinent aquifers, (2) to determine preoperational
water quality in the aquifers, and (3) to assess the impacts of UCG on ground-
water quality.

INTRODUCTION

The first United States field test of in situ or underground coal gasifi-
cation (UCG) were started in 1947 by the U.S. Bureau of Mines (11-14) at
Gorgas, Alabama and lasted through 1958. The overall results of these tests
were disappointing because seam thickness and coal type were not favorable for
UCG. In addition, the economic climate was poor because of the availability
of large quantities of cheap oil and natural gas.

Gulf Research and Development Company (15) conducted a small test in
western Kentucky in 1968. The test produced a very high heating value product
gas for an air injection system, but the reaction was limited to devolatiliza-
tion. The test also showed that air injection pressures above overburden
pressure could be used to enhance the permeability of the coal seam.

The current U.S. program was developed in the early 1970's, but differs
from the earlier programs in being highly instrumented, modeled, and analyzed.
This program addresses coals of different ranks, geographical areas, angles of
dip, operational techniques, and product gas utilization. All processes under
development are designed to complement surface technologies and recover the
resource that is either too thin, deep, or steeply dipping for the conven-
tional recovery methods.

with the WCT Program divided into the Western Low Btu Gas/Air (WLBG) and Western Medium Btu Gas/Steam-Oxygen (WMBG) Projects.

The WLBG Project (1-10) has been conducted by the Laramie Energy Technology Center (LETC) since 1972 near Hanna, Wyoming. The LETC has developed the Linked Vertical Well (LVW) linkage process to increase the permeability of the coal seam. Sandia Laboratories has provided instrumentation and monitoring to LETC since 1974.

The WMBG Project (16-21) has been conducted by the Lawrence Livermore Laboratory (LLL) at Hoe Creek, Wyoming in the Powder River Basin since 1975. LLL has increased the permeability of the coal seam by explosive fracturing, LVW, and deviated borehole drilling.

The ECT Project (22) which is investigating methods of in situ gasification of near market, swelling coals is directed by the Morgantown Energy Technology Center (METC). The CO-Flow Stream Concept developed by METC is planned for field testing in FY 1980 either at its Princetown, West Virginia test site or at an alternate test site yet to be determined.

The SDB Technology (coal seams greater than 35 degrees relative to the earth's surface) is being developed by Gulf Research and Development Company near Rawlins, Wyoming, through a DOE contract (23). This first phase of this project (site selection, characterization, and preliminary design) has been completed, and the first field test is planned for late FY 1980.

There are also some active privately funded UCG projects, but they will not be discussed in this paper.

An integral part of the technology development is a program to determine the potential environmental impacts associated with UCG and the control technology that may be needed not only to meet State and Federal environmental regulations but also for end product utilization. This paper will discuss portions of the environmental programs (groundwater and subsidence) associated with the WLBG and WMBG projects.

The LETC has been investigating the potential environmental impacts associated with UCG at its four UCG test sites near Hanna, Wyoming, (Figure 1) on land made available by Rocky Mountain Energy Company (a subsidary of Union Pacific Railroad). Complementary studies are also being conducted on other types of coal and seams (18-21). Three primary environmental concerns associated with UCG are:

1. Effluent gas quality
2. Surface and subsurface water quality
3. Subsidence effects
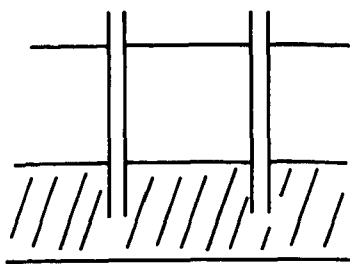
(A) VIRGIN COAL

(B) IGNITION OF COAL

DOWN HOLE
ELECTRIC
HEATER
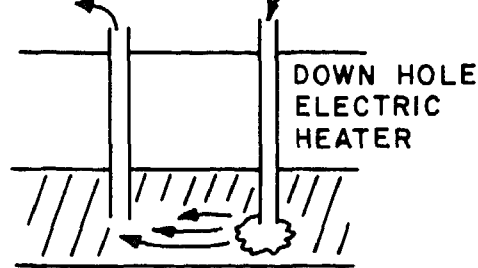
HIGH PRESSURE
AIR INJECTION

GAS
PRODUCTION

LOW PRESSURE
AIR INJECTION

GAS
PRODUCTION
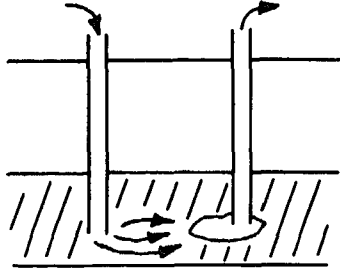
(C) COMBUSTION LINKING
FRONT PROCEEDS TO
SOURCE OF AIR
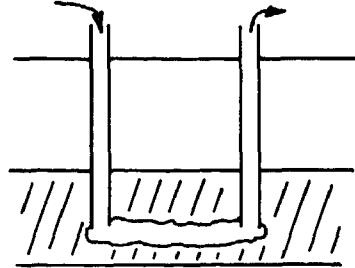
(D) LINKAGE COMPLETE WHEN
COMBUSTION ZONE REACHES
INJECTION WELL (SYSTEM
READY FOR GASIFICATION)

HIGH VOLUME
AIR INJECTION

GAS
PRODUCTION

HIGH VOLUME
AIR INJECTION

GAS
PRODUCTION
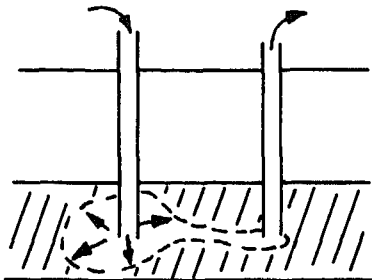
(E) COMBUSTION FRONT
PROCEEDS IN THE SAME
DIRECTION AS INJECTED
AIR
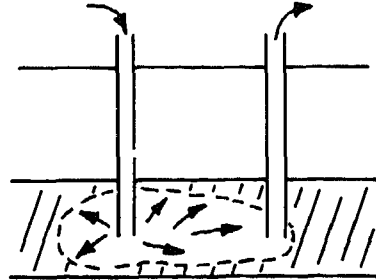
(F) COMBUSTION FRONT EVENTUALLY
REACHES PRODUCTION WELL

Figure 1. LVW Process Description

sustain the fire which moves toward the oxygen source, countercurrent to the air flow. As the fire proceeds, carbonization of the coal produces volatiles and leaves a highly porous, permeable pathway between the wells (D). This preparation process, known as reverse combustion linking, is necessary since virgin coal generally does not have sufficient permeability to allow the high air injection rates needed for efficient gasification. Upon completion of linking, high volumes of air are injected at low pressure (E), expanding the combustion zone towards the initial ignition well where the gases generated during linking and gasification are recovered. This expansion generally has a spherical geometry with some distortion toward the production well due to the presence of the linkage pathway. The expansion of the gasification proceeds at a rate of about 1 to 2 feet per day and grows in width up to two-thirds of the well spacing by the time the front reaches the production well. This results in efficient utilization of the coal between the two wells as shown in (F).

The combustible gases produced are hydrogen, methane, carbon monoxide, ethane and propane. Nitrogen and carbon dioxide are also produced, but have no heating value and dilute the product gas. The process yields 120 to 185 Btu/scf gas. This low-Btu gas can be economically produced (24-26) and efficiently used in a gas-fired turbine or a gas-fired steam boiler to produce electric power.

The Hanna III experiment (5-7) was conducted for approximately seven weeks during June and July 1977. About 2800 tons of coal were gasified during the 38 day gasification period with production rates of up to 10 MM scf/day. The average heating value was 138 Btu/scf with an average thermal efficiency of 78 percent for gasification. Water was added to several of the wells during the gasification phase.

HANNA III OBJECTIVES

The primary objective of the Hanna III experiment was to study the effects of an UCG process on associated aquifers. Three sources of groundwater degradation appear possible. One potential source of degradation results from large amounts of water being removed from the coal as steam with the product gas. This causes the remaining groundwater to carry on increased salt load. Another source of degradation comes from the thermal degradation or transformation of mineral matter within and around the coal seam, with influxing groundwater leaching inorganic salts from these materials thus increasing the inorganic salt load. Organic byproducts produced during carbonization of the coal are swept to the surface with some being left behind as a third source of groundwater degradation. These liquid by-products consist principally of pyridines, phenols, and neutral aliphatic and aromatic hydrocarbons. Any of the organic materials left in the underground system might eventually be dispersed throughout the groundwater regime where communication exists.
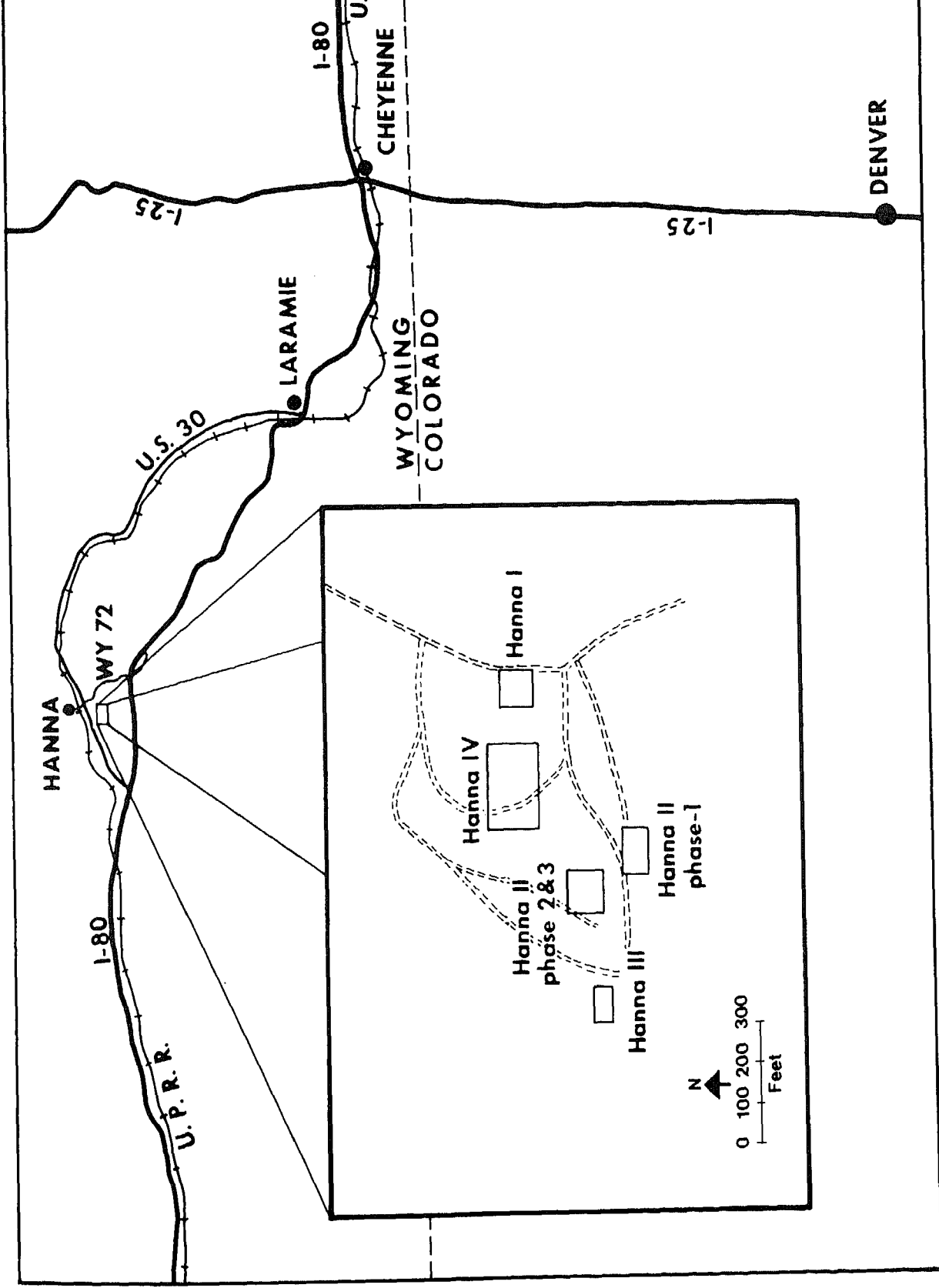
Fig. 2 - LETC's UCG experimental sites

a reasonable time (two to three years). While the gasification experiment was primarily being conducted to allow determination of necessary environmental control strategy, several parameters critical to the process itself were also examined. Table I lists the specific objectives of the Hanna III experiment.

EXPERIMENT

The Hanna III experiment can be divided into three phases:

1. Preoperational (Baseline) - Prior to Julian Day (JD) 157,
2. Operational - JD 157 through 211, and
3. Postoperational - after JD 211

with the operational phase divided into three stages:

a. Start-up - JD 157 through 162,
b. Linkage - JD 162 through 173, and
c. Gasification - JD 173 through 211.

Twelve monitor wells were strategically placed within and downdip from the gasification test area (Figure 3). Wells 1 and 2 were the process wells; wells 3, 4, 5 and 14 were monitor wells for the upper aquifer; and wells 6-13 were monitor wells for the coal seam.

Preoperational monitoring of aquifer characteristics and baseline ground-water quality was conducted. Upon completion of this initial characterization work, wells 1 and 2 were linked by reverse combustion, followed by gasification from well 1 to well 2. During the test, temperature, hydrostatic pressures, and electrical conductivities were continuously monitored in each of the monitor wells. (Continuous monitoring of these parameters were planned during the postoperational phase, but the postoperational burn zone conditions have made these probes inoperable and were subsequently removed). The temperatures and pressures yielded data on water level and temperature changes as a function of both time and process parameters.

Three sets of water samples from each of the fourteen wells in the Hanna III pattern plus three sets from Corehole #4 near the Hanna II site (a well cased and completed to the Hanna #1 seam approximately 800 feet NNE of the Hanna III site) were collected, fractionated, and analyzed, prior to the test. Table II shows the components for which analyses were performed and the fractionation and preservation techniques used. Selected samples were analyzed for the organic constitutents by GC-MS (Gas Chromatography-Mass Spectroscopy).

The well pattern was also designed to obtain the permeabilities and porosities (transmissivities and storage coefficients) and the continuity and directional nature of both the coal seam aquifer and the overlying aquifer. Data on drawdown and pressure build-up tests were obtained by pumping wells 10 and 1 (in turn) for the seam and well 3 for the overlying aquifer.

TABLE I

HANNA III OBJECTIVES

PROCESS

1. TEST PROCESS CONTROL TECHNIQUES

2. DEMONSTRATE PRODUCTION OF CONSTANT HEATING V...
   PRODUCT GAS BY CONTROLLING THE AIR:WATER RATIO
   THE GASIFICATION ZONE

3. IMPROVE THE MATHEMATICAL MODEL

ENVIRONMENTAL

1. CHARACTERIZE THE PROPERTIES OF THE COAL SEAM
   AQUIFER AND OF THE OVERLYING AQUIFER

2. DETERMINE PRE- AND POST-EXPERIMENT WATER QUALIT...
   BOTH AQUIFERS

3. ASSESS THE IMPACTS OF UCG ON GROUNDWATER QUALIT...
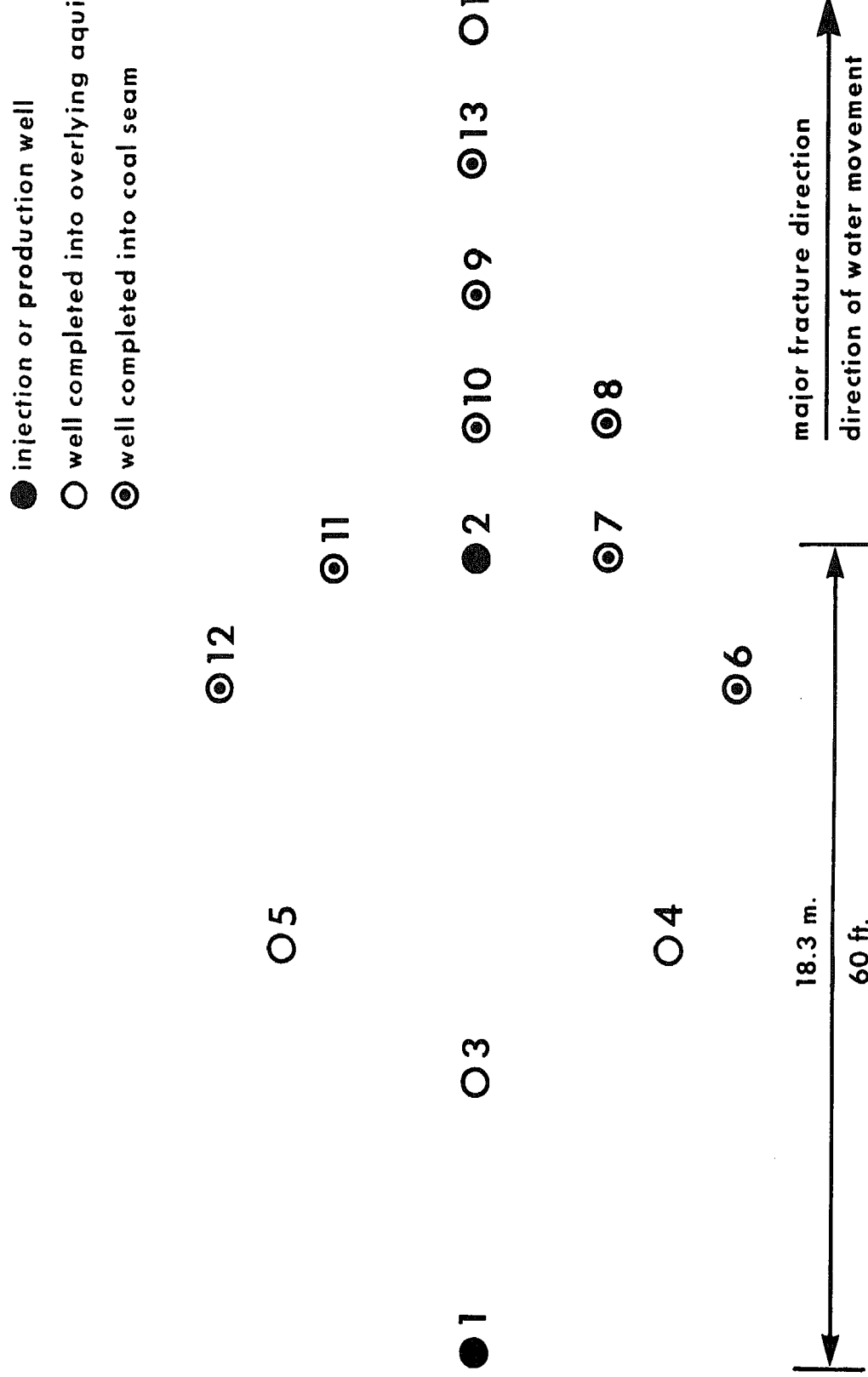
Figure 3. Hanna III

FRACTION	PRESERVATION TECHNIQUE	ANALYSIS
I	COOLED TO 4° C	$SO_4^=$, HCO_3^-, $CO_3^=$, Si, TDS, TOC, B, TOTAL P, F^-, Cl^-, TOTAL INORGANIC CARBON
II	1:8 HNO_3	Na, K, Ca, Mg, Cd, Pb, Zn, Fe, Al, Cu, Mn, Mo, Ti, V, As,
III	1:10 H_2SO_4	NH_3-N, TOTAL N, NO_2^--N, NO_3^--N,
IV	CONC. HNO_3 5% (w/w) $K_2Cr_2O_7$	Hg
V	0.1 M $Zn(C_2H_3O_2)_2$	$S^=$

TABLE II: Hanna III Fractionation and Preservation Techniques

program. This program will continue until sufficient data has been obtained (18-24 months) to determine adsorption rates as a function of time and distance from the source, the extent of the interconnection between the two aquifers, and the groundwater quality changes resulting from migration of leached species.

RESULTS AND DISCUSSION

Preoperational

The initial results of the analyses from the 14 wells at the Hanna III site and from Corehole #4 indicated that the waters contain predominantly sodium bicarbonate. The preoperational samples from the wells at the Hanna III site can be differentiated on the basis of total dissolved solids (TDS) levels and well location, i.e., in the coal seam or in the overlying aquifer. A comparison of some water quality parameters of the two groupings is given in Table III. The samples taken from the coal seam show considerably higher TDS levels and higher concentrations of sodium, bicarbonate, and sulfate.

The composition of these waters was such that they produced a high sodium absorption ratio, which would render them unacceptable for irrigation. The residual sodium carbonate levels were also high and indicated alkali problems would develop if this water were used for long-term irrigation. When the quality of the water in the overlying aquifer is compared to the proposed Wyoming Department of Environmental Quality (DEQ) groundwater quality regulations (27), it meets most of the requirements of a Class V water (is or has the potential for being used as livestock water), but the high concentrations of fluoride and mercury may lower this groundwater to a Class VI (is or has the potential for being beneficially used) or Class VII (the potential for beneficial use shall be determined). The quality of the coal seam aquifer meets the DEQ requirements for a Class III water (has the potential for being used as domestic water), but again the fluoride and mercury concentrations may reduce the groundwater to a Class VI or Class VII. Preliminary results of the organic analyses by GC-MS showed that only one sample (Well 13) contained extraneous organic compounds (28).

Pre-operational drawdown tests showed that the two aquifers were not connected. The undisturbed water level in the coal seam was 120 ft. from the surface while the upper aquifer had water 95 ft. from the surface. Thus, the two zones could be tested independently of each other. The calculated axis of major permeability in the Hanna III site lies 82° east of north. The average permeability for the seam is about 5 md, but the zone is heterogeneous. The upper zone exhibits an even more marked directional nature or heterogeneity, but its average transmissibility is about the same as that of the coal seam (29).

TABLE III

Comparison of the wells at the Hanna III site
(all values reported as mg/l, with the average
given first, followed by the range found)

Parameter	Group 1[a]	Group [b]
TDS (@180°C)	1224 (992-1450)	2614 (181...
Sodium	496 (238-625)	1107 (755...
Carbonate	33 (0-181)	25 (0-21...
Bicarbonate	1131 (799-1280)	1774 (127...
Sulfate	35 (1-143)	679 (244...
Total Inorganic Carbon	224 (204-248)	364 (328...
Fluoride	1.8 (1.0-3.2)	1.04 (.8...
Ammonia (as N)	1.1 (.9-2.1)	1.7 (1.0...
Boron	0.03 (<0.01-0.11)	0.08 (0...
Total Organic Carbon	41 (31-51)	11 (9-12...

[a] Wells 1, 2, 6, 7, 8, 9, 10, 11, 12, 13 and Corehole 4.

[b] Wells 3, 4, 5 and 14. (Overlying Aquifer)

ment. There was no pressure response in the overlying aquifer during linkage, but responses were observed during gasification. Well 3 responded first, as expected, and within ten days responses were observed in the other wells completed into the overlying aquifer.

The temperature remained constant (45-55°F) during the start up and linkage phase. During gasification temperature increases of about 50°F were observed at wells 6 and 12 from JD 178 to 200, and then at wells 7, 10, and 11 from JD 200 to 204. No temperature changes were observed at wells 8, 9, and 13. This sequence of well response follows the gasification progression from well 1 to 2. (There were no coal seam thermocouples to track the burn progression as in the other Hanna experiments.) Temperature increases in the overlying aquifer (well 3) were observed on JD 198 (Figure 4) which indicated breakthrough into the aquifer. No temperature responses in the other wells were observed.

The conductivity probes indicated changes in loading level in wells 9 and 13 during start up. This response probably resulted from the ignition and air injection into nearby well 2, and the production gases following a more permeable zone leading towards wells 9 and 13. During the link, the conductivity of the water in the coal seam aquifer remained constant, and during start up the conductivity of the overlying acquifer remained constant. It is apparent from both the previously discussed linkage temperature data and this conductivity data that the linkage path did not intersect or come close enough to the temperature or conductivity probes to generate a response.

During gasification conductivity responses were observed within the first five days at wells 9 and 13. These wells were also the first to show conductivity responses during start up. Production gases from the gasification zone probably again followed a more permeable zone to these wells. Well 10 located between wells 2 and 9 responded on JD 203. Wells 7, 8, and 11 remained constant. Increased conductivity levels were observed at well 3 in the overlying aquifer on JD 187 (Figure 4) indicating product gas seepage into the overlying aquifer. Wells 14 and 4 responded approximately five days later, but well 5 remained constant. (Anemolies were observed in the well 5 probes since they were installed).

Hydrostatic pressure, conductivity, and temperature responses at well 3 were observed on JD 184, 187, and 198, respectively. The pressure response indicated that there was communication (fissures and coal shrinkage) between the coal seam and the overlying aquifer. As the gasification cavity increased in size and overburden sluffing continued, additional fractures penetrated into the overlying aquifer allowing product gas into the aquifer resulting in conductivity increases. Finally, on JD 198 additional roofall caused communication between the gasification zone and the overlying aquifer.

Wells 6 and 12 showed opposite temperature and conductivity responses. The temperature increased, remained constant for three weeks (JD 178-200), and returned to its original level. Three days later the conductivity probes
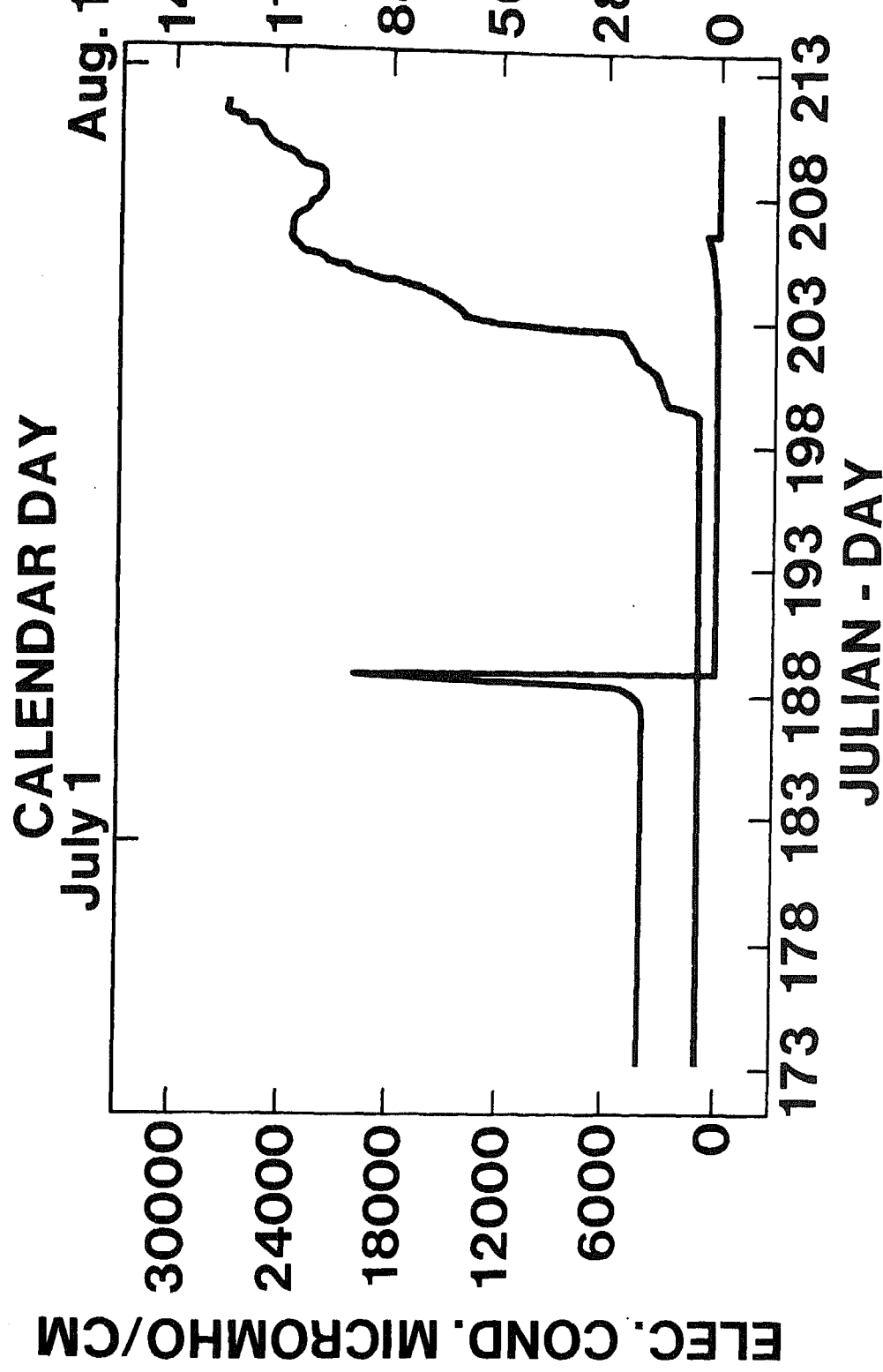
Fig. 4 - Downhole Conductivity and
Temperature Responses for Well #3

Postoperational

Early postoperational hydrostatic pressure, temperature, and conductivity data have not been analyzed and interpreted due to computer data retrieval problems. This data will be retrieved and analyzed in the near future.

Preliminary results from the first month's postoperational water quality monitoring appear to indicate that the sulfate and chloride concentrations are decreasing and sodium and total dissolved solids are increasing in all wells. Organic characterization data are not yet available.

CONCLUSIONS

Preoperational water quality data indicates that the natural groundwater would be unacceptable for short and long term irrigation, and when the quality is compared to the proposed Wyoming Department of Environmental Quality Groundwater Regulations, it may only meet the requirements for a water that has the potential for beneficial use.

Preliminary results indicate that UCG does have an impact on the groundwater. As the monitoring program and data analysis and interpretation progresses, the extent of the environmental impacts will be determined. Once these impacts are known, control and/or utilization technology will be determined.

ACKNOWLEDGEMENTS

The authors acknowledge Dennis D. Fischer, R. Michael Boyd, A. Eugene Humphrey, S. Bruce King, and David L. Whitman, all formerly of LETC, for their contributions to the UCG program.

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LLL INVESTIGATIONS OF GROUND-WATER AND SUBSIDENCE EFFECTS*

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ABSTRACT

The conversion of coal into combustible gases promises to become an important method of coal utilization. If this conversion is carried out with the coal in place underground - in situ coal gasification - additional environmental and economic advantages can be realized. Our investigations are designed to evaluate some of the environmental implications of this alternative energy technology, and to identify appropriate environmental controls.

Changes in ground-water quality and the possible effects of subsidence and ground movement induced by the underground gasification cavity represent significant environmental concerns associated with the in situ gasification process. We have measured these effects at the sites of two in situ coal gasification experiments conducted in northeastern Wyoming by the Lawrence Livermore Laboratory. Our measurements of ground-water quality in the vicinity of the gasification experiments indicate that the reaction products, such as ash and some coal tars, that remain underground following gasification, are a potential source of localized ground-water contamination. However, the concentration of important contaminants, such as phenols, show a significant decrease due to adsorption by the surrounding coal. Complementary laboratory measurements are providing detailed information concerning this adsorption process.

We have also conducted laboratory and field measurements, in conjunction with modeling studies, to evaluate the effects of subsidence phenomena. Data from subsurface geotechnical instruments installed at the second gasification experiment, as well as measurements of ground-water levels, indicate that roof collapse connected the gasification cavity with overlying aquifers. The environmental implications of this interconnection are being investigated. Our results suggest that hydrogeological site-selection criteria may be of considerable environmental importance in choosing locations for commercial-scale operations.

gasification promises to become an important method of coal utilization. If the gasificaton of coal is accomplished with the coal in place underground - in situ gasification - additional environmental and economic advantages can be realized. For example, in situ coal gasification can be carried out without the need for underground mine workers, and it may make recovery of very deep coals economically attractive.

In situ coal gasification generally involves a complex series of chemical reactions, but it can be simply characterized as the heating of coal in the presence of gasifying agents such as oxygen and steam. Some of the coal is burned to provide heat to drive the gasification reactons. In the simplest form of in situ gasification, two or more process wells drilled into the coal seam are used, after the coal is ignited, to inject air or other gasifying agents and to withdraw the resulting combustible gas mixture (Fig. 1). In most cases, the coal's permeability must be enhanced, before gasification, along a path connecting the process wells. (The need to achieve this preliminary connection reliably and economically represents an important current challenge in the development of a practicable in situ technology.) The product gas generally requires some form of clean-up in a surface plant and, if synthetic natural gas is the desired product, an upgrading process to achieve higher energy density.

Although in situ coal gasification offers important environmental advantages when compared with more conventional methods of coal utilization, there are significant environmental concerns that need to be investigated. If these concerns are addressed now, in parallel with the development of the in situ method, it will be possible to identify appropriate control technologies in a timely manner and, perhaps, influence process development such as to preclude or minimize adverse environmental effects.

In order to insure that realistic and effective control methods will be identified, it is essential to develop a quantitative understanding of potential environmental effects as they would occur in connection with large, commercial-sized operations. Some of these possible effects are peculiar to underground gasification and have not been previously investigated in detail. Futhermore, important environmental consequences may require decades to develop. We are therefore concentrating our present efforts on the accumulation of basic data concerning the potential sources of environmental effects, and on the development of reliable, predictive modeling capabilities. With this background, it should be possible to isolate control technologies that are realistically applicable to this promising method of coal recovery.

Two characteristic features of the in situ coal gasification process have led to particular environmental concern: first, the fact that some of the reaction products remain underground as potential ground-water contaminants and, second, the cavity (and possible subsidence) produced by the extraction of the gasified coal. Our in situ coal environmental group at the Lawrence
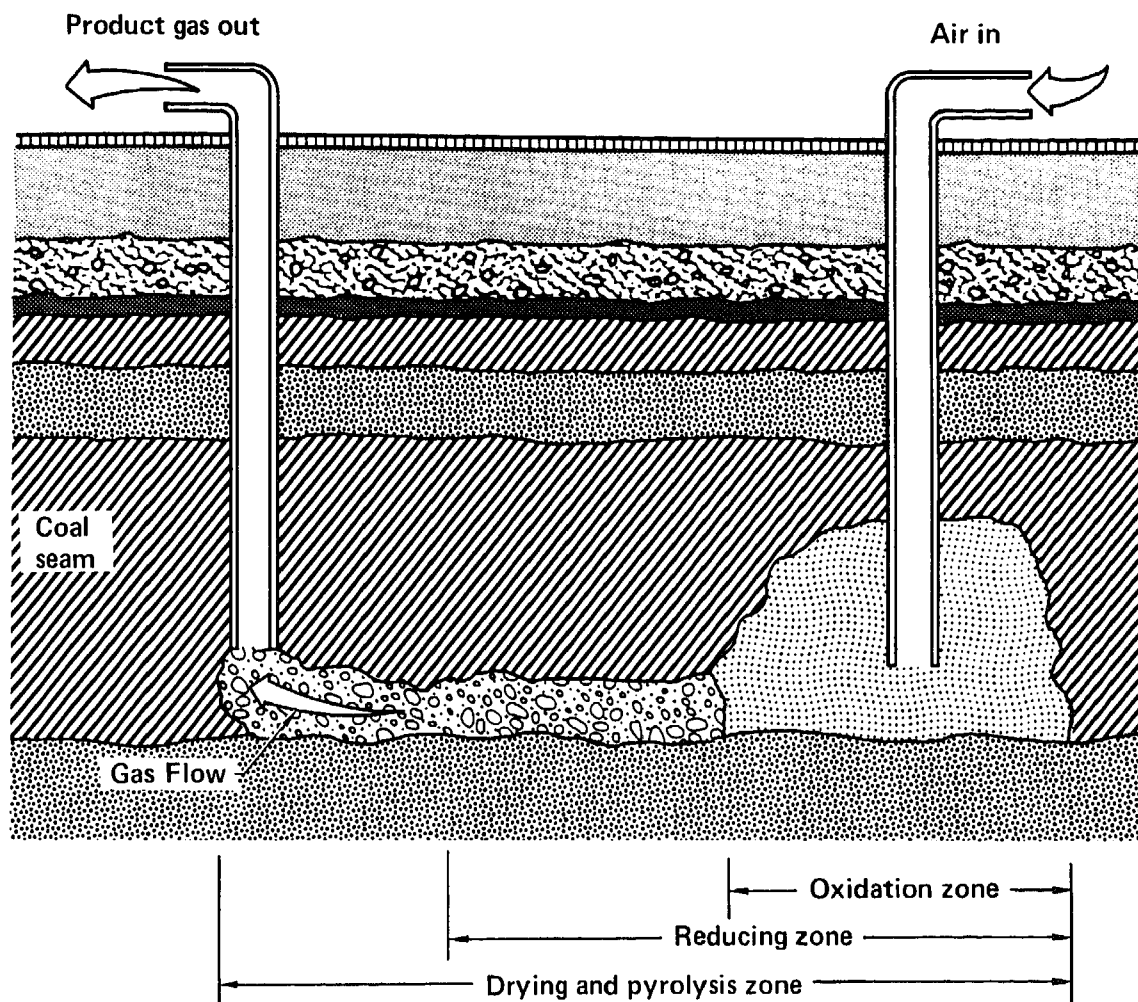
Figure 1.   Schematic representation of the *in situ* coal gasification process. The region ahead of the oxidation zone has been modified before gasification to provide a path of increased permeability that will permit adequate gas flow.

consequences. Our approach involves a combination of field measurements near in situ gasification experiments, laboratory investigations, and predictive modeling studies.

LLL has conducted two in situ coal gasification experiments[1,2] at its Hoe Creek site in northeastern Wyoming. These experiments have given us the opportunity to measure changes in ground-water quality and subsidence effects associated with two underground gasification operations.

The Hoe Creek site is located in a sparsely populated region of gently rolling semi-arid rangeland. This area is part of the Powder River basin of northeast Wyoming and southeast Montana - a region that may contain half a trillion tons of coal suitable for in situ gasification. The coal gasified in the Hoe Creek experiments (the Felix II Coal) is 25 ft thick and lies at a depth of about 125 ft - well below the static water level. The Felix II Coal is an aquifer and is overlain by two additional aquifers. A detailed evaluation of the hydraulic characteristics of the Felix Coal and the near-by strata at the Hoe Creek site will be found in reference 3.

The first Hoe Creek experiment[1] took place in the fall of 1976. The two process wells - for injecting air and extracting product gas - were about 33 ft apart, and chemical explosives were used to produce enhanced permea-bility in the Felix II coal. Approximately 120 tons of coal were gasified in an 11-day experiment.

A second experiment, Hoe Creek II, was conducted during the fall and winter of 1977. The process wells were located approximately 60 ft apart and the required path of enhanced permeability was achieved using a preliminary "reverse combustion" technique, developed in this country by the Laramie Energy Technology Center. The gasification operation lasted 58 days, during which approximately 2000 tons of coal were converted to gas and extracted through the production well. The average energy content of this gas was 108 Btu/scf. Gas losses during this experiment averaged 20%.

Perhaps the most significant environmental concern associated with the underground gasification of coal stems from the existence of gasification reaction products that remain underground. These residual materials include coal ash, char, some of the coal tars, and approximately 10-15% of the product gases which are not extracted through the production wells. When ground water returns to the gasification zone, the ash is leached, producing inorganic contaminants, and some of the other residual materials, including organics are dissolved. The contaminated water moves through the coal seam in the general direction of the natural ground-water flow. Fortunately, there are other natural phenomena - for example, the filtering and adsorption properties of coal itself - which tend to purify the ground water and to restrict the contaminants to a localized region. Nevertheless, the ultimate environmental significance of the residual underground products is not yet known.

in part, because these phenomena may affect the dispersal of the reaction-product contaminants. In particular, fissuring and roof collapse, which result from cavity formation, can destroy the integrity of the underground "reaction vessel" and permit the escape of pollutants to the surface or into overlying aquifers. Large areal gasification operations could also lead to significant surface subsidence, with results that may be important environmentally, and in their effects on process facilities.

WATER SAMPLING AT HOE CREEK I

Measurements of changes in ground-water quality near in situ coal gasification experiments are of importance, initially, in that they help to define the contaminant source. That is, they permit a description of the composition, concentration, and early-time distribution of the underground contaminants. Such measurements also provide information concerning short-term changes in concentration and composition that are a result of chemical reactions, sorption by coal and other media, or biological action. Over a period of several years, the water quality measurements will begin to yield information concerning the possible development of a plume of contaminated ground water that may spread outward from the gasification site in the direction of natural ground-water flow.

We have carried out extensive ground-water quality investigations at the sites of both LLL in situ coal gasification experiments. Approximately a dozen wells in the vicinity of the first gasification experiment (Hoe Creek I) were monitored before, during, and after gasification.[4,5] The samples were analyzed in the field and, much more extensively, at the laboratories of the U. S. Geological Survey, the Research Triangle Institute, and LLL. A simplified summary of the data is given in Table I.

Species	Pre-gasification value (mg/l)	Inside burn zone Concentration Increase (mg/l)		Outside burn zone Concentration Increase (mg/l)	
Phenols	0.001	0.1	100 x	500	5×10^5 x
CN^-	0.01	0.4	40 x	300	3×10^4 x
NH_4^+	0.5	20	40 x	70	100 x
DOC	6	4	-	200	40 x
Br^-	0.1	1.0	10 x	4	40 x
Pb^{+2}	0.001	0.001	-	0.04	40 x
Ba^{+2}	0.1	-	-	1.0	10 x
K^+	5	60	10 x	45	8 x
Li^{+1}	0.03	0.3	10 x	0.2	6 x
Mg^{+2}	10	50	5 x	60	6 x
SO_4^{-2}	200	2000	10 x	1000	5 x
Ca^{+2}	40	600	20 x	200	5 x
B (III)	0.1	0.7	7 x	0.5	5 x

Among the chemical species that show a large increase as a result of the gasification experiment are the phenolic materials, which represent the largest group of organic contaminants introduced into the underground environment by this experiment. The changes in concentration of the phenolic materials, as a function of time and distance from the boundary of the gasified zone, are shown in Fig. 2. Notice that the phenol concentrations have decreased by roughly two orders of magnitude at all distances from the burn zone. Although most other contaminants are also decreasing[5], their rates of decrease are not, in general, as rapid as those indicated in Fig. 2.

The water from selected wells was analyzed by the Research Triangle Institute using a method that combines gas chromotography and mass spectrometry (GC-mass spec). This technique (now also employed at LLL) provides detailed information concerning volatile and semi-volatile organic contaminants. The coal gasification process produces an enormous variety of such organic by-products. The more volatile aromatic materials such as benzene, toluene, xylenes, and napthalene penetrate into the porous media surrounding the gasification zone.[5] As illustrated in Fig. 3, the species of lower molecular weight (more volatile) are transported further from the gasification zone. A discussion of some limitations that apply to quantitative comparisons of the GC-mass spec data with results obtained by other methods will be found in Ref. 5.
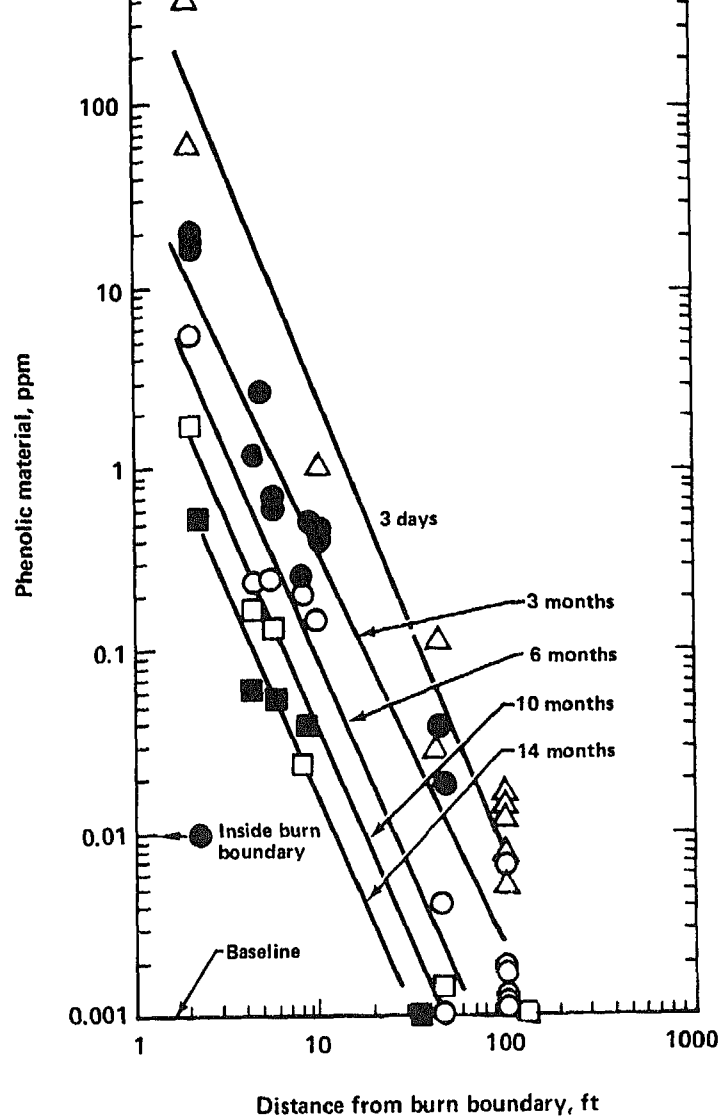
Figure 2.   Concentrations of phenolic materials as a function of distance from the nearest burn boundary of the Hoe Creek I *in situ* coal gasification experiment. Times are measured from the end of gasification. Sampling wells are completed in the gasified coal seam and located in various directions from the gasification zone.
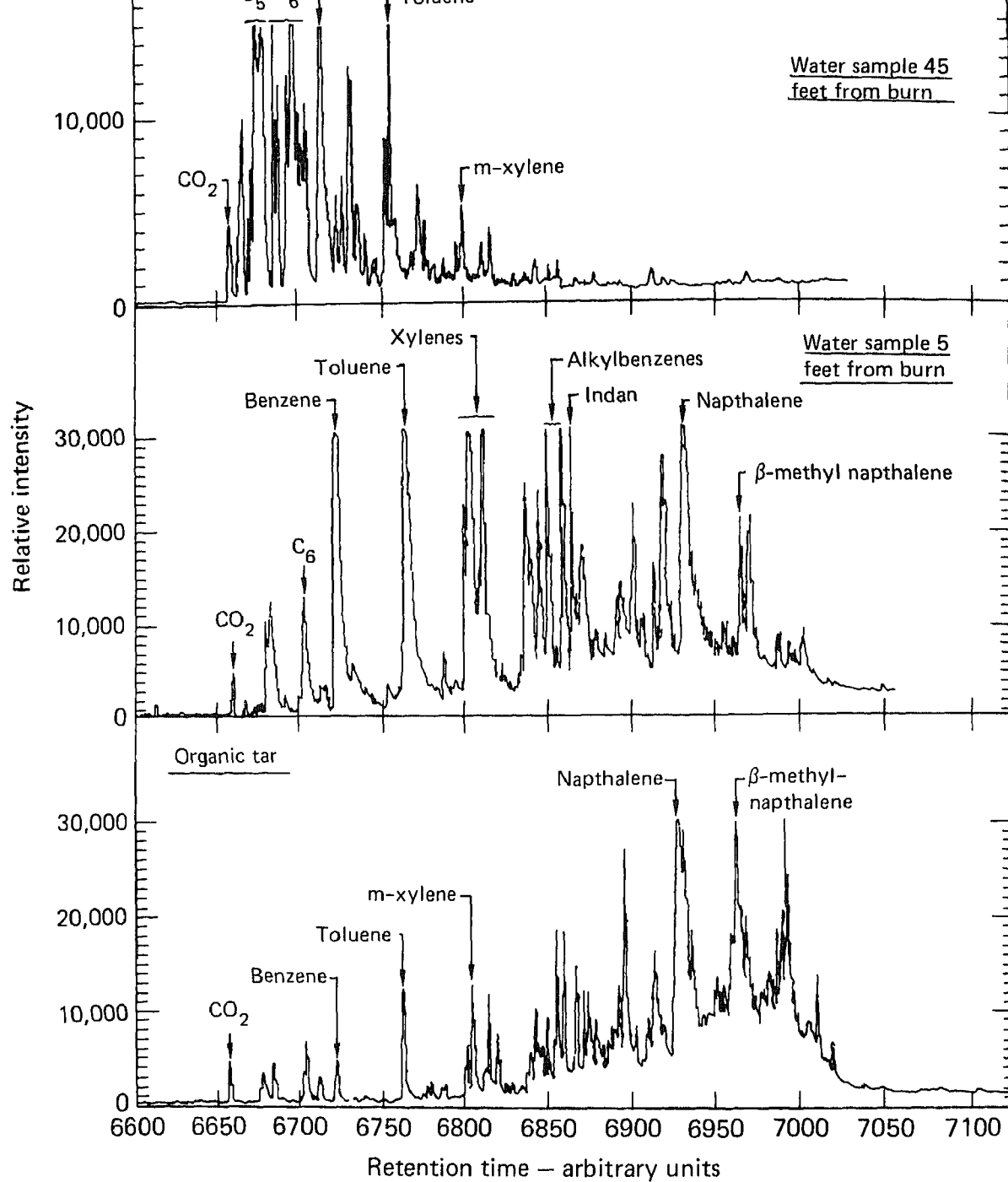
Figure 3. Chromatograms of volatile organics found in product tar and in water obtained 5 ft and 45 ft from the burn zone. The numbers on the abscissa are related to the chromatograph retention times. Note that the lower-molecular-weight (more volatile) species move much further out into the formation, and that the organics in the nearby water are more like the product stream tar.

year. Consequently, data such as those presented in Fig. 2 do not, as yet, provide evidence concerning changes in contaminant concentrations that may occur as a result of natural ground-water flow. In principal, phenol concentrations in the outer wells might ultimately increase. Nevertheless, the rapid and uniform decrease in the concentrations of phenolic materials over a period of more than a year is an encouraging example of the self-cleansing capabilities of coal aquifers.

LABORATORY AND COMPUTATIONAL STUDIES

A clearer and more quantitative understanding of the ground-water changes near an underground gasification operation can be achieved by means of laboratory investigations carried out in conjunction with the field measurements. Of particular interest, are the nature and magnitude of the cleansing actions that occur when contaminated water is exposed to coal. Results such as those shown in Fig. 4 leave little doubt that phenol is rapidly adsorbed by coal. More elaborate experiments involving the flow of contaminants through a column of coal (Fig. 5) are also underway. They establish values of the distribution coefficient, K_d, which is a measure of the fractional adsorption of a dissolved contaminant and an essential ingredient in contaminant transport modeling. Our modeling efforts include the development of a 2-dimensional computer code capable of predicting transient dispersion of contaminants introduced continuously from a line source. The model includes convection, longitudinal and lateral dispersion, and adsorption.[6]

GROUND-WATER EFFECTS AT HOE CREEK II

Nine ground-water sampling wells were provided for measuring ground-water quality changes resulting from the second Hoe Creek experiment. Since the second experiment involved the gasification of 20 times as much coal as Hoe Creek I, it would be of considerable interest to compare ground-water changes near the two sites. Such a comparison might help to establish the dependence of the contaminant source strength on the amount of coal gasified. In particular, the comparison might indicate whether the concentrated "shell" of phenolic materials just outside the burn zone is a surface effect or dependent on the entire gasified volume. Unfortunately, a straightforward and meaningful comparison of ground-water measurements at the two sites is impossible, for reasons discussed below.

We have sampled the ground-water near the Hoe Creek II site before, during, and several times after gasification. Some analyses are performed in the field, and preserved samples are sent for extensive analysis to U.S. Geological Survey laboratories, Gulf South Research Institute, and LLL. The

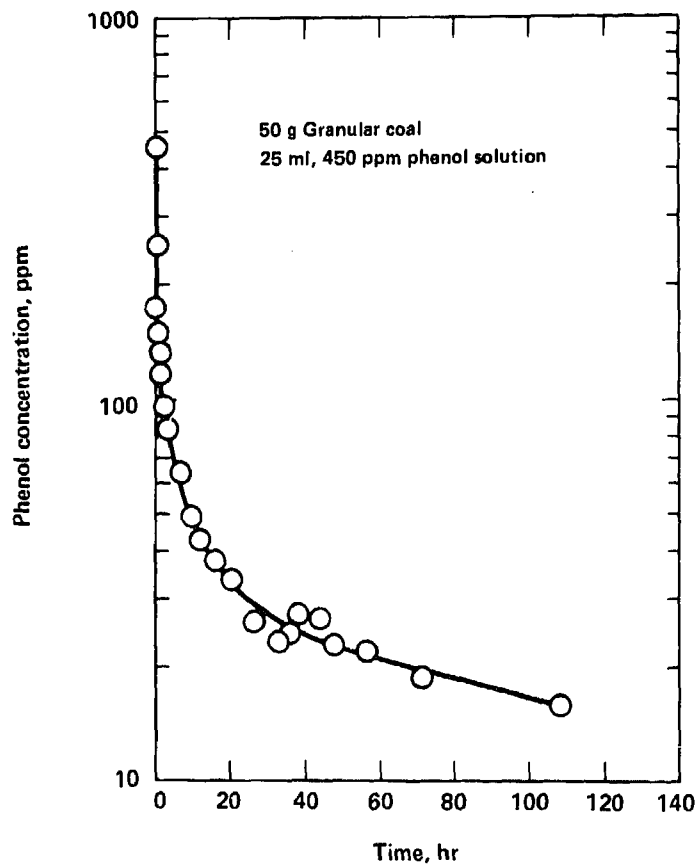Figure 4. Laboratory measurements of phenol adsorbed by granular coal as a function of time. The data represent the analysis of a large number of equivalent phenol solutions agitated with a shaker table.
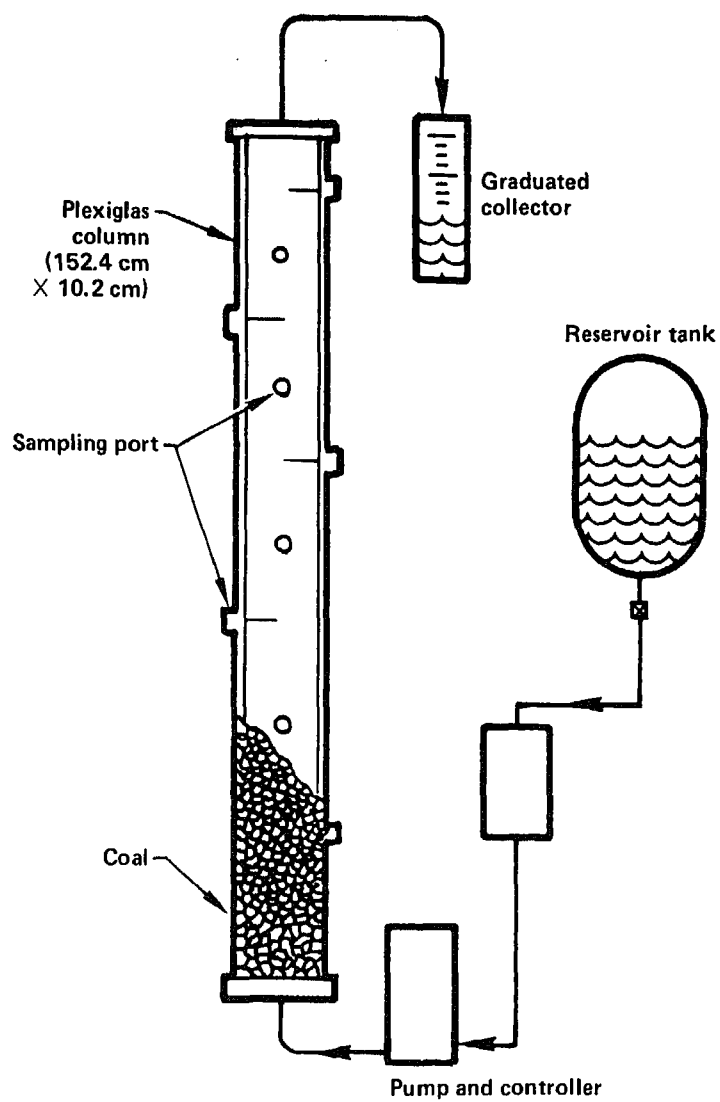
Figure 5.   Coal column apparatus used to simulate the flow of
contaminated ground water through a coal seam.
During operation, samples are extracted through
rubber septa using a hypodermic syringe.

of more than 400 ppm near the Hoe Creek I experiment. Of course, the phenol concentrations are expected to depend very strongly on well locations relative to the burn boundary (Fig. 2), and this effect could account for large differences in measured concentrations. However, a more important difference stands in the way of a simple comparison of contaminant levels near the two sites. Water level data (Fig. 6), subsurface geotechnical measurements, and post-burn coring investigations show that cavity roof collapse connected the gasification cavity with overlying aquifers (The Felix I Coal and a coarse channel sand above it). Since the Hoe Creek site is a recharge area (hydraulic head decreasing with depth), water from the overlying aquifers is flowing into the gasification cavity and producing an abnormally high hydraulic head within the cavity. Calculations based on the data of Fig. 6 suggest that ground-water flow rates in the immediate vicinity of the cavity exceed normal flow rates by at least an order of magnitude. Preliminary data on phenol concentrations (Fig. 7) showed a temporary increase in concentration in some of the sampling wells, which are completed in the Felix II Coal. Evidently, source concentrations and source geometry were significantly affected by the aquifer interconnection. The environmental implications of the altered contaminant distribution are being investigated.

Another question whose importance is emphasized by the aquifer interconnection at the Hoe Creek II site concerns the possibility that contaminants from the gasification zone may migrate into overlying aquifers. Additional sampling wells recently completed in the Felix I aquifer will help to answer this question. It may be that the downward flow of water in a recharge area will minimize the spread of contaminants into overlying aquifers. In any case, the importance of an enlightened choice of site selection criteria is becoming increasingly apparent.

SUBSIDENCE STUDIES

Since ground deformations induced by the gasification cavity may play an important role in determining contaminant dispersal and may, in addition, lead to significant surface subsidence, an improved understanding of these subsidence phenomena is of outstanding importance. We are attempting to extend out knowledge of these effects and develop a reliable predictive capability through a combination of laboratory tests of overburden cores, geotechnical measurements at the site of ongoing gasification experiments, and finite element modeling.

A preliminary modeling study of the subsidence induced by underground coal gasification was conducted in preparation for the first Hoe Creek experiment.[7] In the treatment employed, a stratified overburden is stressed by gravity loading and by the removal of coal seam elements in a manner simulating coal combustion. The resulting stresses, strains, and displacements are determined for the duration of the excavation process and for subsequent quiescent periods during which plastic deformation and stress relaxation gradually take place in the rock and soil strata. Inelastic
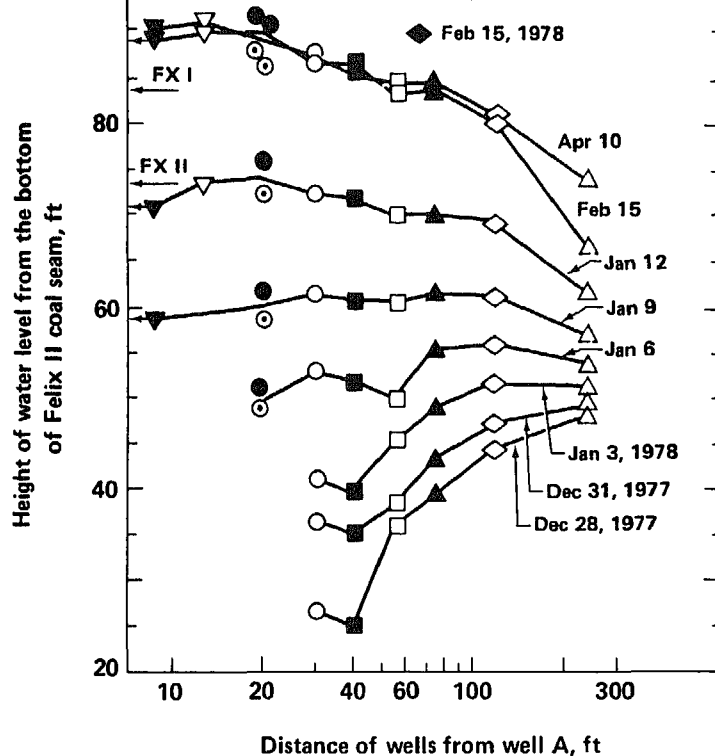
Figure 6. Water levels in wells near the Hoe Creek II *in situ* coal gasification experiment. The water levels are plotted as a function of distance from the injection well "A" at various times following gasification. (A logarithmic distance scale is used to avoid data crowding for the close-in wells.) All wells are completed in the gasified Felix II coal seam except WS-1, which was completed in the overlying Felix I coal aquifer. The data show how water levels have changed since air injection was terminated at the conclusion of the gasification experiment on December 25, 1977. The elevated water levels in the vicinity of the gasification zone suggest that the gasification cavity has been interconnected with the overlying Felix I coal aquifer, which lies about 20 feet above the Felix II Coal, and with another aquifer above the Felix I Coal.
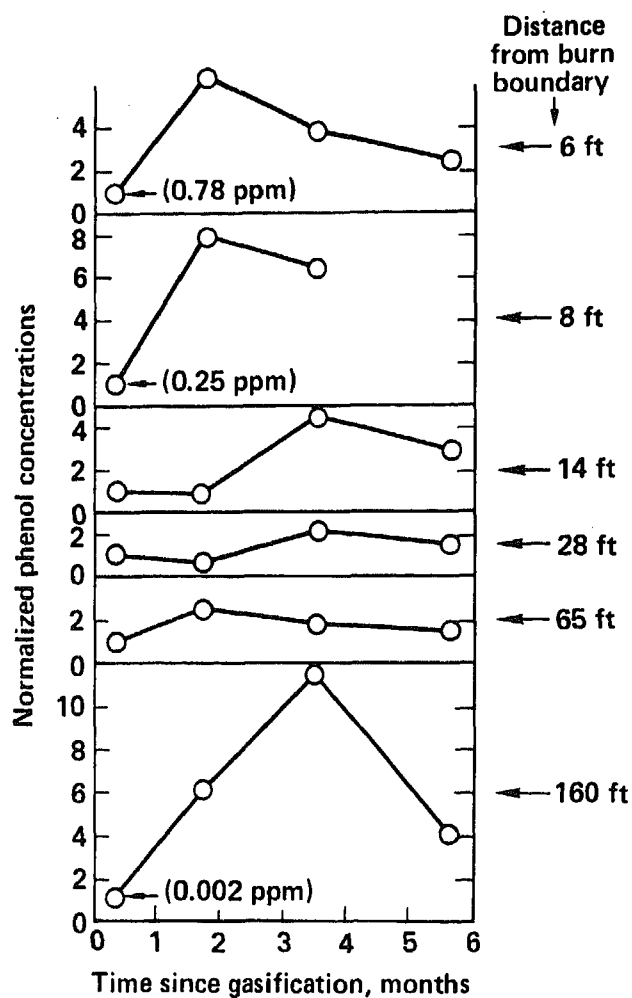
Figure 7. Changes in the measured concentrations of phenolic materials in the Felix II coal aquifer as a function of time after gasification. The measurements were made in some of the wells shown in Figure 5. These and other data suggest that the contaminants are moving outward away from the gasification zone. This movement appears to be much exaggerated in the immediate vicinity of the gasification zone as a result of an interconnection with an overlying aquifer. (Note that the actual magnitudes of the phenol concentrations measured in the close-in wells are hundreds of times greater than those in the outermost well.)

Within the accuracy of our surface-monument measurements, no post-burn surface subsidence was detected.

An augmented version of the above method was used in an effort to predict subsidence and ground movement for the Hoe Creek II experiment.[8]   Two sets of assumed values of material properties were employed, termed "probable" and "lower bound". We also added a new feature to our method of modeling the excavation process associated with gasification. As the computations proceeded, roof material that developed tensile stress was mathematically removed in a subsequent iteration. In other words: as coal elements were "gasified" and zones of tensile stress appeared in the roof, those zones were "spalled" or allowed to collapse. This procedure produces a shallow arched roof, free of tensile stress, such as might be expected to occur naturally.

This augmented model also predicted surface subsidence of only an inch or so. On the other hand, relatively large deformations, and considerable roof caving were predicted below the surface. It seemed clear that subsurface measurements would produce the most helpful data - both for understanding the implications of subsidence for the in situ gasification process, and as a guide in checking and improving our subsidence modeling capabilities. Subsequent measurements have shown that a combination of roof caving and combustion (in the overlying Felix I Coal) caused portions of the cavity to be extended some 70 ft above the top of the Felix II Coal, much higher than predicted.

In an effort to provide subsurface data, we designed an array of geotechnical instruments for installation in the overburden at the site of the Hoe Creek II experiment (Fig. 8). The instruments included two 6-position borehole extensometers (Fig. 9), two electrical shear strips, a multiple pie-zometer installation, and a borehole deflectometer apparatus that was utilized in six specially cased boreholes. Provisions for surface measurements included specially designed isolation bench marks, an optical level, and a precision tape extensometer. A detailed description of these instruments, their deployment at the Hoe Creek II site, and some preliminary results are reported by Ganow et al. in reference 9.   An analysis of the geotechnical data (obtained before, during, and after the Hoe Creek II experiment) has provided a relatively clear picture of the overburden deformation and roof collapse that occurred in response to the growth of the gasification cavity. Of particular interest, is the fact that the extensometers and piezometers documented the interconnection of the gasified coal seam with the overlying Felix I and channel sand aquifers.

Since a variety of measurements have shown that roof collapse extended significantly higher than predicted, we are attempting to develop modeling methods that take account of process-related phenomena that may be significant. Roof spalling due to shrinkage effects induced by heating may be an important factor in determining the utlimate cavity size. A preliminary attempt to incorporate these shrinkage effects into the calculations is described by Greenlaw et al. in reference 10.
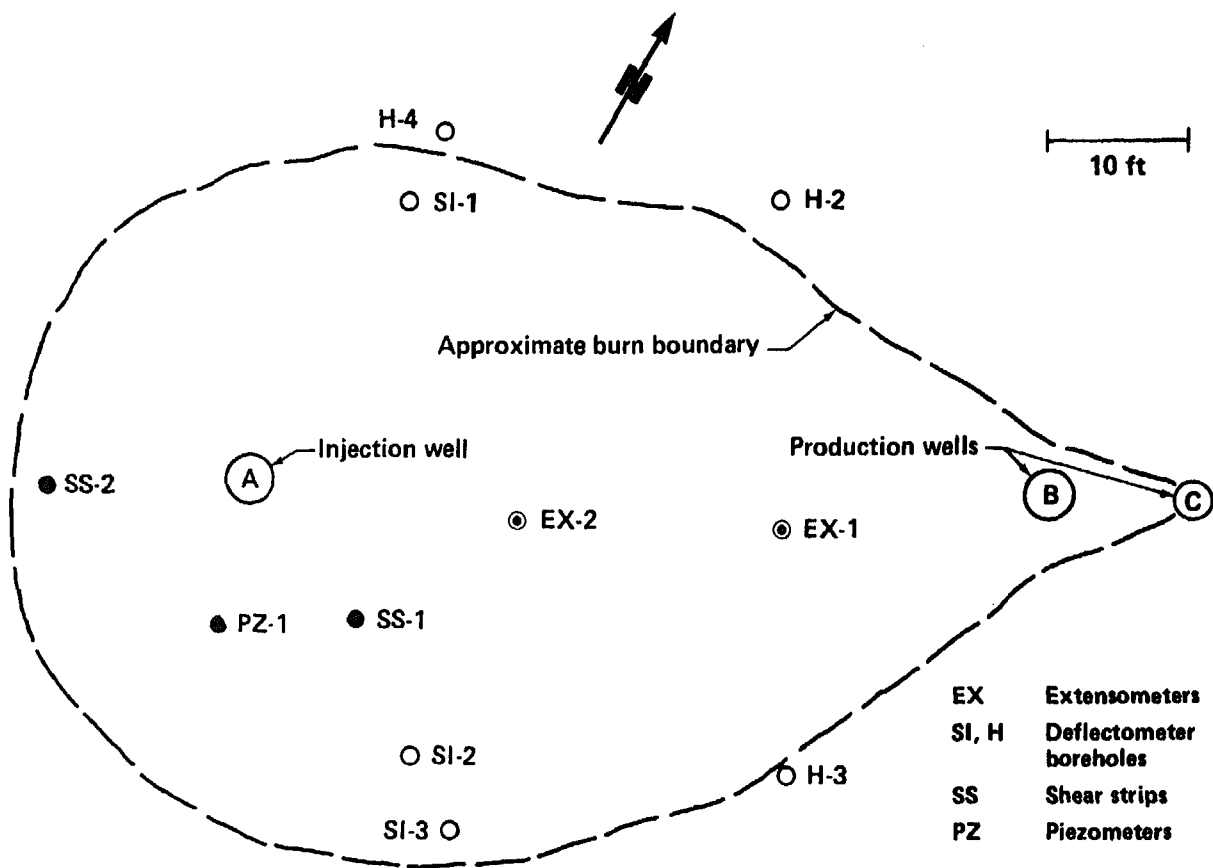
Figure 8.   Plan view showing process wells and subsidence instrumentation boreholes at Site II.

Top plate

Pulley

Sensing
wire

Transducer
(linear resistor)

Sensing wire

Guide rod

Plastic
weather
case

Followers clamped
to sensing wire
and to moving element
of transducer

Lead
counter
weight

Follower in full
extension position

Base plate

Weld

Well casing
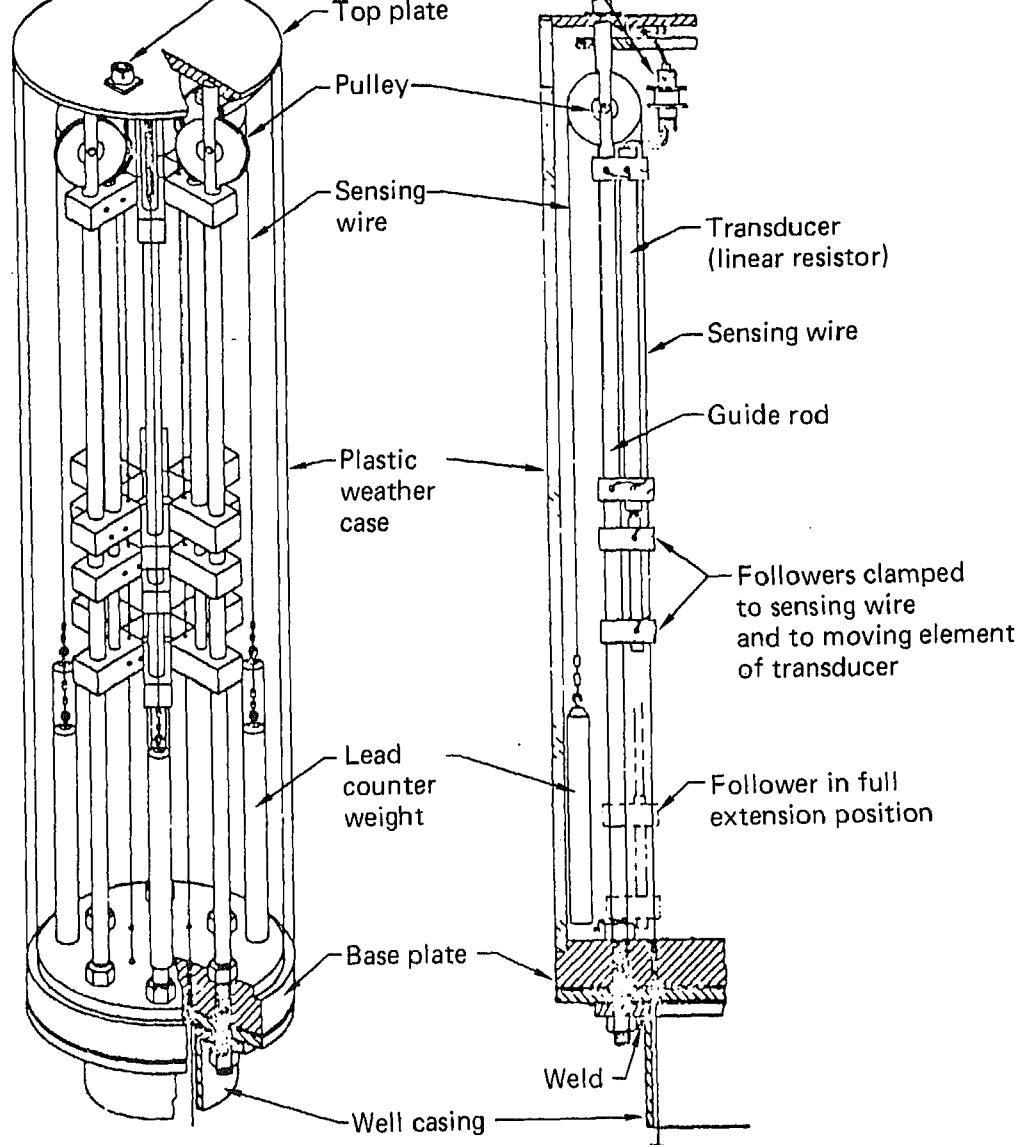
Figure 9.   Multiple-position borehole extensometer sensing head. Cables from the sensing head extend down to expandable mechanical anchors located at various positions in the overburden. Displacements measured at the sensing head are the integrals of vertical strains occurring between the head and the various anchor points.

obtained from these tests will be used in future modeling studies.
The usefulness of 3-dimensional solutions will also be explored. We are
hopeful that an improved knowledge of subsidence behavior in actual
gasification experiments, used in conjunction with properly measured
overburden characteristics, can permit the development of predictive modeling
capabilities that will be a reliable guide to the subsidence phenomena that
may accompany large scale in situ coal gasification.

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1. INTRODUCTION

High temperature entrained flow coal gasifiers have a well-known advantage over lower temperature fixed-bed or stirred-bed gasifiers. This advantage is the marked reduction in tars, phenols, and other condensible hydrocarbons as gasifier by-products. For example, Lurgi fixed-bed gasifiers produce from 50-100 pounds of tar, 30-70 pounds of tar oil and naptha, and 8-12 pounds of phenols per ton of coal (1,2). Similar by-product compounds and yields have been reported for a fluidized bed gasifier operated by the Pittsburgh Energy Research Center (3). On the other hand, the Koppers-Totzek and Texaco High temperature entrained flow gasifiers are claimed to produce negligible amounts of tars and oils as by-products. The gas and water purification equipment is, therefore, less complicated and less expensive than that required for the Lurgi process. It was anticipated that more advanced high temperature entrained flow gasifiers would also have this advantage.

The experimental gasifier studied in this report is housed at the Eyring Research Institute in Provo, Utah. This gasifier is a pressurized, entrained-flow gasifier that has a capacity of ~50 pounds of coal per hour and has a downflow configuration with some similarity to an entrained flow gasifier operated by the Bureau of Mines during the period 1952-1963. It also has some similarity to the Texaco entrained flow gasifier configuration.

2. PROCEDURE

A diagram of the laboratory gasifier and the necessary coal feeding, gas cooling and cleaning, and ash handling equipment is shown in Figure 1. Pulverized coal from a pressurized feed hopper is fed to the gasifier entrained in a stream of recycle gas. The coal is rapidly mixed and reacted with a mixture of super-heated steam and oxygen. The reaction is carried out at pressures of 75 to 150 psig and gasifier outlet temperatures of 2300-2800°F. Residence times for gasification reactions are of the order of 0.1 second.

The gasifier products pass downward into a quench section where they are

Fig. 1.   Flow Diagram of Laboratory Scale Gasifier

Designation	Description	
V101	Coal lock vessel	18" × 57"
V102	Coal feed vessel	18" × 57"
V201	Gasifier section	10" × 12"
V202	Ash/slag accumulator vessel	10" × 4'
V203	Ash/slag lock hopper	10" × 3'
V301	Steam drum	4" × 4', 18 kw heater
V401	Scrubber column	10" × 4'
V601	Recycle gas inlet vessel	12" × 6'
V602	Recycle gas accumulator	14" × 6'
V701	H.P. water accumulator	10" × 3'
E201	Oxygen heater	3/8" × 40' coil, 5 kw
E202	Steam superheater	3/8" × 40' coil, 5 kw
E203	Steam evaporator	3/8" coil
E204	Economizer exchanger	19 tubes, 3/8" × 2'
E301,2	Condensors	5" × 24"
E401	Scrubber water cooler	60,000 BTUH
F401,2	Scrubber liquor filter	8" × 34", 4.4 sq. ft.
F501,2	Product gas filter	4" × 24"

of soot and fly-ash particles from the gas is accomplished.

In this study, a detailed characterization of products and by-products associated with this gasifier was performed. Four process parameters, as shown in Table 1, were varied; coal feed rate, reactor pressure, oxygen to coal ratio, and steam to coal ratio. A high-volatile, non-caking, Utah bituminous coal was used for most of this study. A simplified flow chart showing the gasifier effluent streams is shown in Figure 2. Samples were taken from the cooled and water-scrubbed product gas stream, the scrubber effluent water, and the gas evolved on depressurization of the scrubber water. The gas samples were analyzed by gas chromatography and selective reaction indicator cartridges while the scrubber water was subjected to the analysis scheme shown in Figure 3. The scrubber water was first filtered to remove the particulate matter. Portions were then analyzed by proton induced x-ray emission (PIXE) and atomic absorption spectroscopy, thermometric titrimetry, and ion chromatography. Both the filtered scrubber water and the particulate matter were extracted with methylene chloride and analyzed by gas chromatographic mass spectrometry.

Table 1

Gasifier Test Parameters

Reactor Pressure (psia)	75	150	
Coal Feed Rate (lbs./hr.)	20	40	60
Oxygen to Coal Ratio (wt/wt)	0.8	0.9	1.0
Steam to Coal Ratio (wt/wt)	0.1	0.3	0.5

3. RESULTS

Analysis of effluent streams at median gasifier conditions. The data in Tables 2 through 5 represent the average of three gasifier test runs that were made under identical reactor conditions: coal feed rate = 40 lbs. of Utah bituminous coal/hour, reactor pressure = 150 psia, oxygen to coal ratio = 0.9, and steam to coal ratio = 0.3. Table 2 shows the product gas composition. Gases which were specifically tested for and not found at the sensitivity level of 0.5 ppm include SO_2, COS, NH_3 and CS_2. The composition of the flash gas obtained during depressurization of the scrubber is given in Table 3. Again, SO_2, COS, NH_3, and CS_2 were not detected.

Table 4 shows the net elemental composition of the scrubber water after subtraction of concentration levels measured in the water before scrubbing. PIXE analysis can detect nearly any element between atomic numbers 14 and 40 above an approximate detection limit of 0.5 ppm. The detection limits for heavier elements are somewhat higher. Notice that the data are given both in units of ppm in scrubber water and lbs per ton of coal feed. It was found impossible to compare our data with data from other gasifiers because of the inavailability of certain gasifier operating parameters.
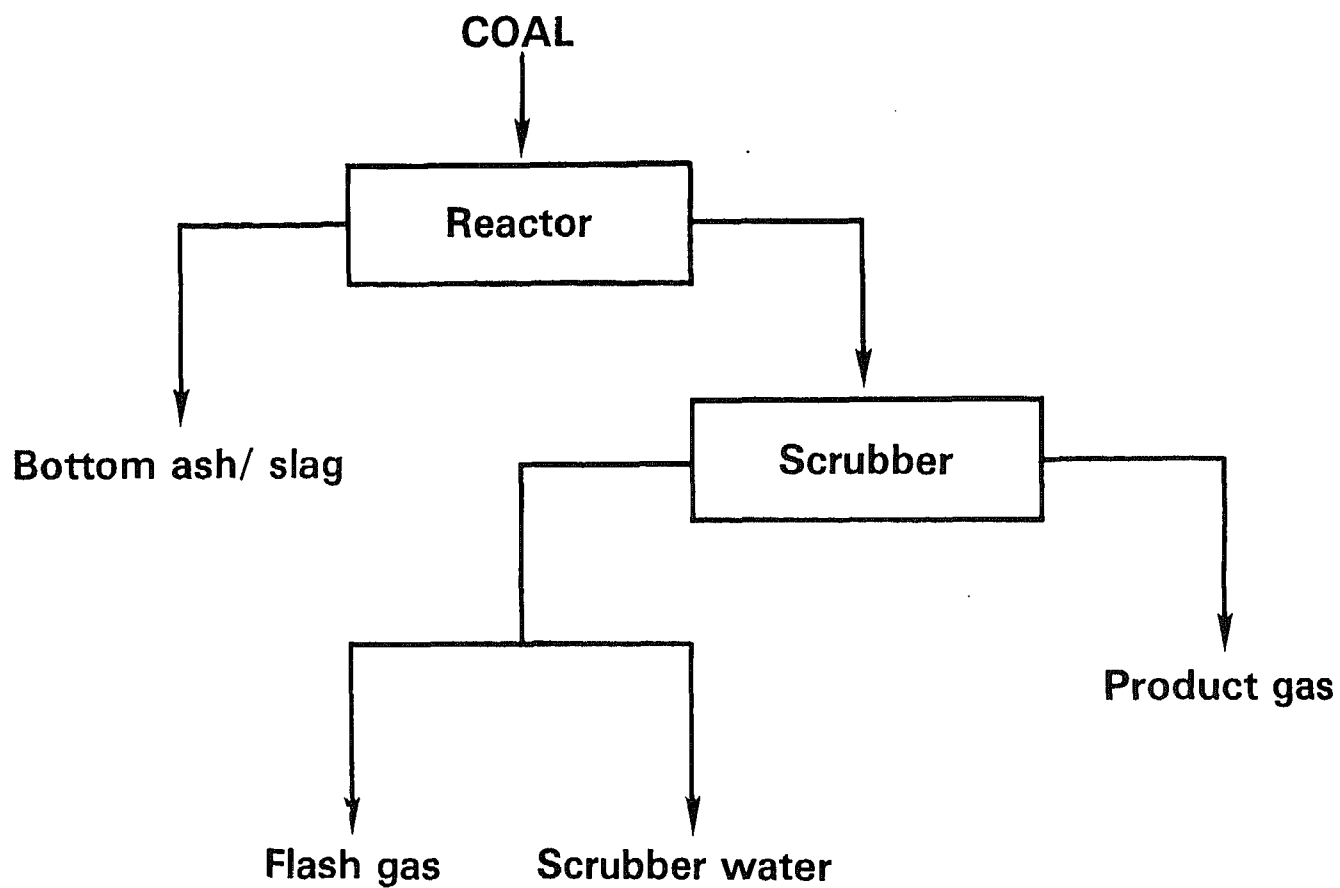
Fig. 2. Gasifier Product and Effluent Streams
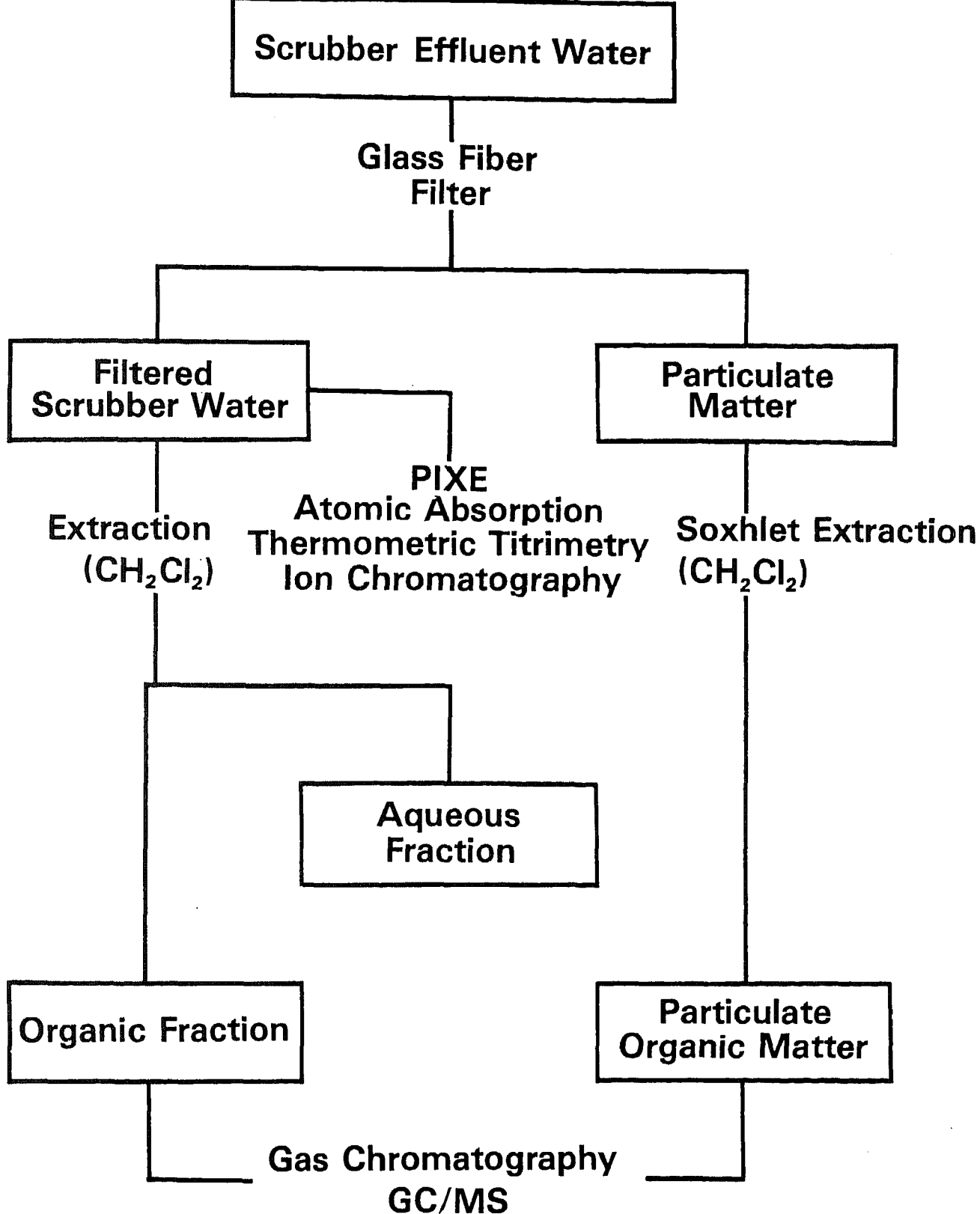
Fig. 3. Flow Diagram of Scrubber Water Analysis Procedure

Gas	(Volume)	lbs/ton Coal
CO	54%	2300
H_2	30%	88
CO_2	11%	690
N_2	5%	200
CH_4	0.7%	15
H_2S	550 ppm	3
HCN	1 ppm	0.004

Flash Gas	(Volume)	lbs/ton Coal
CO_2	31%	14.0
N_2	34%	9.9
CO	31%	8.9
CH_4	0.4%	0.6
H_2S	0.4%	0.14
H_2	4%	0.007
HCN	44 ppm	0.001

Table 4

Filtered Scrubber Water Elemental Composition

Element	ppm	lbs/ton of Coal
Ca	50	4.6
S	8	0.78
Si	3	0.28
Fe	2	0.22
Cl	3	0.30
Zn	1	0.13
K	1	0.09
Sr	0.3	0.03

Table 5

Filtered Scrubber Water Inorganic Species

Species	ppm	lbs/ton of Coal
HCO_3^-	210	19.0
Cl^-	9	0.85
F^-	1	0.11
NH_4^+	45	4.12
NO_3^-	0.6	0.03

Cu, Ti, Mn, Ni, Br, Hg, Se, and As detected at same level both before and after scrubbing.

Other elements ($14 \leq Z \leq 40$) not detected (<0.5 ppm).

SO_4^{2-} and SO_3^{2-} detected at same level both before and after scrubbing.

Carboxylic acids, phenols, and amines not detected (<5 ppm).

The reporting of data in terms of weight per weight or weight per volume of pollutant in scrubber water is important from an environmental standpoint, but nearly useless for quantitative gasifier production comparisons because of the variability in scrubber water flow rates. In fact, an effluent stream can appear to be quite clean when data is presented in terms of ppm, when in reality the seemingly low levels of pollutants are a direct result of a very fast scrubber water flow rate. For this reason, we report quantitative data both in

Table 5 shows the inorganic species identified in the scrubber water by ion chromatography and thermometric titrimetry. Species not detected and approximate sensitivity levels are shown.

An interesting aspect of this study was the analysis of the organic compounds present in the scrubber water. After filtering 1.5 liters of the scrubber water through a 1.2μ pore filter, extracting 2 times with 100 ml each of methylene chloride, evaporating almost to dryness, and injecting the total amount into a gas chromatograph, essentially no organic compounds were found. On the other hand, the methylene chloride extract of the particulate matter which was filtered from the scrubber water contained significant amounts of organic compounds, all of which are polycyclic aromatic hydrocarbons. Figure 4 shows a capillary column gas chromatogram of the organic extract of the particulate matter of one sample. All peaks represent fused-ring aromatic systems. The absence of alkylated compounds is expected from a high temperature system.

There is only approximately 1×10^{-3} lbs. of extractable organic material in the unfiltered scrubber water per ton of coal consumed, and the total amount is quantitatively adsorbed on the particulate matter. Natusch (4) has recently presented a theoretical model describing the quantitative adsorption of polycyclic aromatic hydrocarbons onto fly ash due to the sudden decrease in temperature as the fly ash exits from the stack of a coal-fired power plant. It appears that the same process is occuring as the product gas stream is cooled by the spray of water in the scrubber column. We tested the adsorption of naphthalene on particulate matter in water by dissolving 15 mg of naphthalene in one liter of distilled water which was thermostated at 22°C and successively adding portions of previously extracted particulate matter. After each addition, the amount of naphthalene adsorbed was determined by UV absorption. Figure 5 shows the adsorption curve obtained. Notice that 100% adsorption will be obtained at approximately 0.40 ppt particulate matter in the water. Scrubber water from the gasifier typically contained about 2% particulate matter so there is clearly sufficient to adsorb all of the organics from the water.

From the data in Tables 2-5 it may be concluded that (1) the effluent streams from this type of gasifier are extremely clean when compared to other types of gasifiers, (2) all of the nonvolatile organic compounds produced are quantitatively adsorbed by the particulate matter in the scrubber water, and (3) the only potential pollutants from the gasifier other than the soot in the scrubber water and the bottom ash/slag are the H_2S and HCN in the product and flash gases and NH_4^+ in the scrubber water. The HCN is present in such small amounts that it probably is not environmentally significant.

Effects of gasifier conditions on effluent streams. Table 6 summarizes the significant effects of changing the gasifier operating conditions. Decreasing the pressure in the gasifier from 150 psia to 75 psia decreased the CO output per ton of coal by a factor of about 1.5. This is a large loss of coal conversion efficiency. The output of HCN, polycyclic aromatic hydrocarbons as represented by naphthalene, and scrubber collected soot all increased.
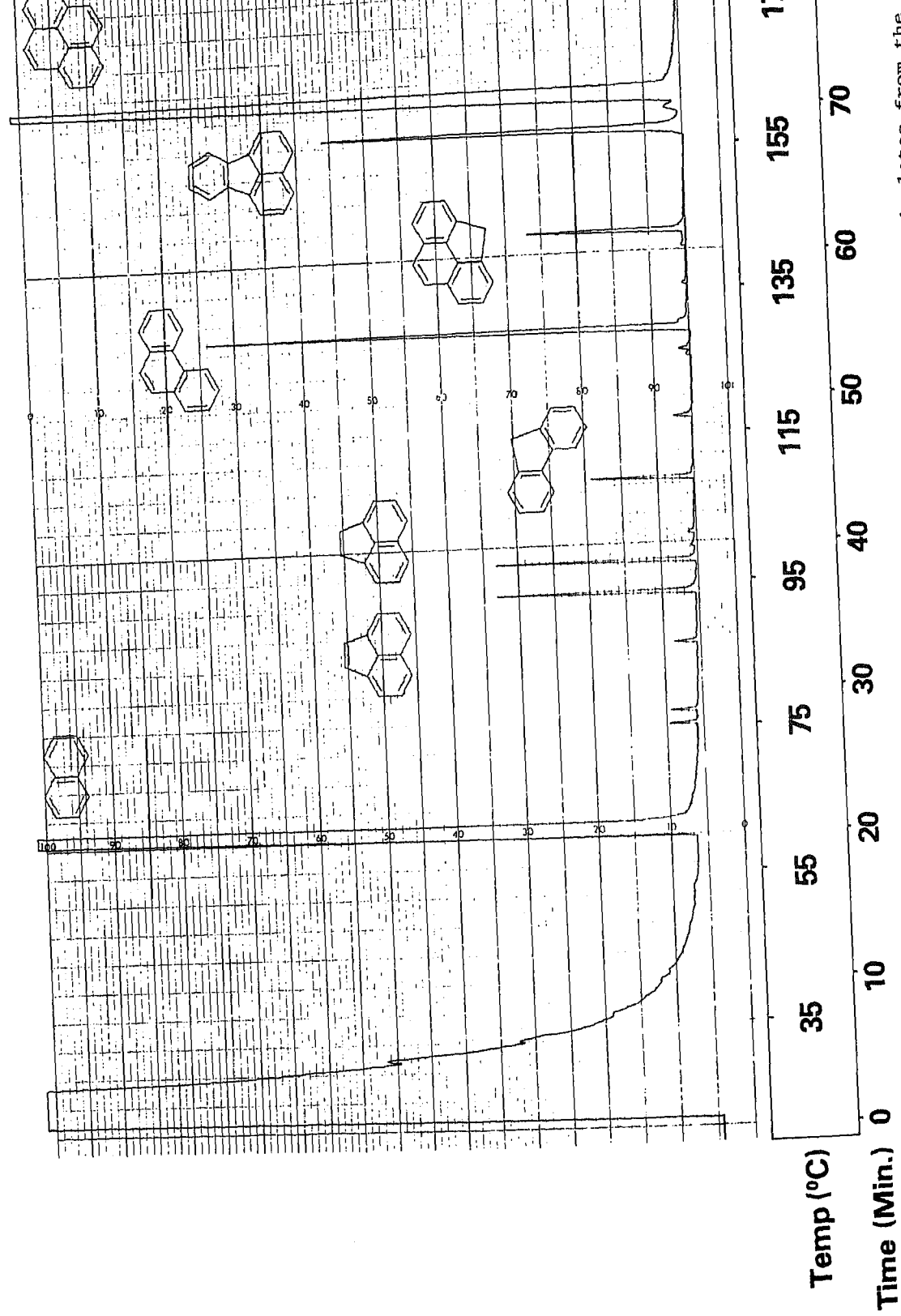
Fig. 4. GC Separation and MS Identification of Polyciclic Aromatics in Particulates from the

Temp (°C)   35   55   75   95   115   135   155

Time (Min.) 0   10   20   30   40   50   60   70
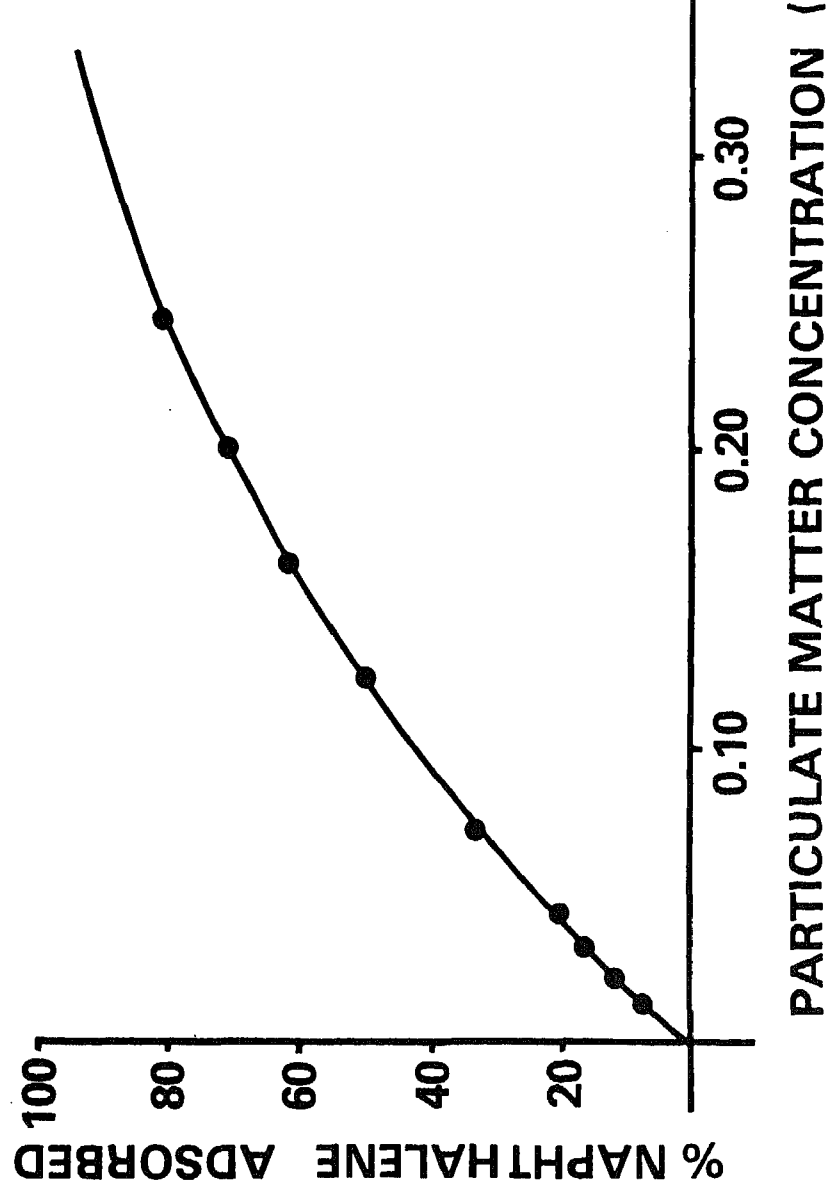
Fig. 5. Adsorption Isotherm for Naphthalene on Particulate Matter from the

	Decreasing Pressure 150 75 psia	Decreasing Coal Feed Rate 60 → 40 → 20 lbs/hr	Decreasing O_2/Coal 1.0→0.9→0.8 lb/lb	Decreasing Steam/Coal 0.5→0.3→0.1 lb/lb
		Product Gas		
CO	decrease x 1.5[a]	No effect then decrease x 1.8[a]	c	c
H_2	c	c	c	c
CH_4	increase x 2[b]	dec.-inc. x 4[b]	increase x 4[a]	c
H_2S	c	c	decrease x 4[a]	c
HCN	increase x 6[b]	c	c	c
		Flash Gas		
CO	c	c	c	c
H_2	c	increase x 7[b]	c	c
H_2S	c	c	c	c
HCN	increase x 3[b]	c	c	c
		Scrubber Water		
NH_4^+	c	increase x 2[b]	c	decrease x 2[b]
Total naphthalene on soot	increase x 7[a]	decrease x 3[b]	c	c
Soot	increase x 4[a]	decrease x 5[b]	c	c

a. Most significant changes.
b. Not significant in comparison to other changes.
c. No effect.

These results suggest that operating at pressures higher than 150 psia may result in better coal conversion efficiency and lower outputs of these pollutants. Attempts to run at higher pressures in the present gasifier resulted in mechanical problems, however.

Decreasing the coal feed rate below 40 lbs/hour also caused a large decrease in CO production. In this case production of naphthalene and soot were decreased.

Decreasing the O_2/coal ratio in the reactor produced the only significant decrease in H_2S found. Changing the O_2/coal ratio from 1 (wt/wt) to 0.8 re-

the H_2S and increasing the methane in the product gas.

In conclusion, higher pressures and lower O_2/coal ratios should be studied to see if the trends observed in this study continue to change with the gasifier parameters.

Sulfur chemistry. The whole question of the reactions of sulfur in the gasifier is an important area for further research. About 25% of the sulfur in the coal ends up as H_2S in the product and flash gases, another 10% ends up dissolved in the scrubber water as ionic species, and the remaining two-thirds of the sulfur is present in the bottom ash/slag and scrubber collected soot. The chemical state and fraction of the sulfur in the bottom ash/slag is unknown at present. The particulate sulfur collected in the scrubber is elemental sulfur which is tightly bound in the soot matrix. Sulfur was removed from the soot at a constant rate by Soxhlet extraction of the soot with CH_2Cl_2 for several days. Such extractions never appeared to be complete.

The elemental sulfur in the soot is probably formed by oxidation of H_2S by oxygen containing groups on the surface of the graphitic soot particles. Similar behavior of activated charcoal which has been exposed to oxygen has been observed in other studies.[5] The presence of peroxides in the scrubber water was also inferred from the results of thermometric titrations of acidified scrubber water with $Cr_2O_7^{2-}$. An understanding of these reactions could lead to new methods for scrubbing H_2S from gas streams.

The soot produced in this gasifier and collected in the scrubber water thus serves two beneficial functions: (1) the quantitative removal of polycyclic aromatic hydrocarbons from the water and (2) the partial removal of H_2S from the product gas.

Gasification of other carbonaceous fuels. Preliminary experiments on other types of coal, lignite, and COED char indicate that gasifier conditions can be adjusted to gasify these fuels as cleanly as the bituminous coal.

5. CONCLUSION

If economical and simple means can be found to remove the residual H_2S from the product and flash gases and the soot from the scrubber water, this type of gasifier has the potential of supplying clean gas from coal with very little environmental impact on water on air quality.

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ACKNOWLEDGEMENT ,

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INTRODUCTION

Increasing demands for natural gas and oil, partly caused by needs for environmental protection, have led to the inevitable situation where demand exceeds the U.S. productive capacity. The trade deficit from importing these clean fuels plus the uncertain political situation in the Middle East have prompted a drive for energy self-reliance in the United States.

Coal is a dirty, cumbersome fuel whose use in the past has been extensive, often with unfavorable consequences to the environment. Nevertheless, coal constitutes over 70% of the total estimated ultimately recoverable fossil fuel resources in the U.S. and will obviously be important in meeting future energy demands.

Besides being directly fired in boilers for generating steam to drive turbines and provide process heat, coal may be used for producing chemicals and clean fuels. Coal is used throughout the world as a raw material for synthesis of fertilizers and chemicals. This production generally uses a gasification system, such as Lurgi, Koppers-Totzek, or Winkler, to generate synthesis gas (usually hydrogen or a mixture of hydrogen and carbon monoxide).

Koppers-Totzek technology has had commercial application in at least 12 countries since 1955. The Texaco gasification process, which has been tested with coal at the semi-commercial scale and has operated commercially with oil in over 20 countries since the 1940's, is planned for commercial application in combined cycle power plants.[1]

Potential emissions from entrained flow coal gasifiers, such as the K-T and Texaco, are presented in this paper. Commercial control systems for treatment of potential emissions are discussed relative to their applicability to entrained flow gasifiers.

DESCRIPTION OF GASIFICATION TECHNOLOGIES

Commercial, or near commercial, coal gasifiers that employ an entrained flow contacting method include the Koppers-Totzek (K-T) gasifier, the pressurized K-T, and the Texaco gasifier. Description of these gasifiers are presented in the following discussion.

of Mines at Louisiana, Missouri. The pilot plant was operated for two years to produce liquid fuels from coal.

The first commercial plant employing Koppers-Totzek gasification was completed in Finland in 1952.[2] Since that time, plants have been built in Spain, Japan, Belgium, Portugal, Greece, United Arab Republic, Thailand, East Germany, Turkey, Zambia, and South Africa.[2,3] Plants at other locations are currently under construction.

The K-T process employs the partial oxidation of pulverized coal in suspension with oxygen and steam. The Koppers-Totzek gasifier, shown schematically in Figure 1, is a refractory-lined steel shell cooled with a steam jacket to produce low-pressure process steam. Coal, oxygen and steam are fed to the gasifier through opposing special metering heads or nozzles. Coal is pulverized to 70% through a 200 mesh screen and dried to from 2 to 8% moisture. Exothermic reactions create temperatures of 3300-3500°F at the gasifier outlet. About 50% of the ash is entrained with unburned carbon in the fuel gas while 50% flows down the refractory walls into a water quench at the base of the gasifier. Less than 2% of the coal carbon accompanies the ash streams. Flux is sometimes added to the coal to adjust ash fusion properties, such that the slag flows freely from the gasifier and does not solidify on the refractory wall.[2,3]

Two-headed K-T gasifiers with opposing nozzles 180° apart are capable of gasifying about 400 tons/day of coal to produce 15,000 scfm of gas. The capacity is essentially doubled in four-headed units with two sets of opposing nozzles 90° apart. The larger two-headed units are 10 to 12 ft in diameter, tapering to 6 to 8 ft at either end; overall vessel length is 25 ft. with an inner volume of about 1000 ft^3. Four-headed gasifiers have similar dimensions and double the inner volume.[2,3]

Operational experience has shown that the gasification reactions can be controlled by monitoring the CO_2 concentration in the product gas. The CO_2 level indicates the extent of chemical reaction, and controls are adjusted to maintain the CO_2 concentration within a preselected range. Typical results using a K-T gasifier are given in Table 1.

The flow diagram depicted in Figure 2 shows schematically equipment used for synthesis gas production. The fire-tube boiler is inclined from the exit of the radiant boiler to a venturi scrubber. High-pressure steam (up to 1500 psig) is generated in the boiler. The gas from the boiler passes to a two-stage venturi scrubbing system where the particulate level is reduced to 0.002 to 0.005 grains/scf.[2] Large particles (95% of total) are removed in the first fixed venturi. A second adjustable venturi scrubber removes 99% of the remaining particles. After particulate removal, the gas is cooled to about 95°F with water in a packed tower. As in early designs, the gas is then compressed for sulfur removal.

Cooling and scrub water are recycled in a circuit shown schematically in Figure 2. Slag quench water is cooled to prevent evaporation losses, and makeup for water lost with the slag is provided from the cooling and scrub water circuit. Makeup water for the system is added to the packed cooling tower.
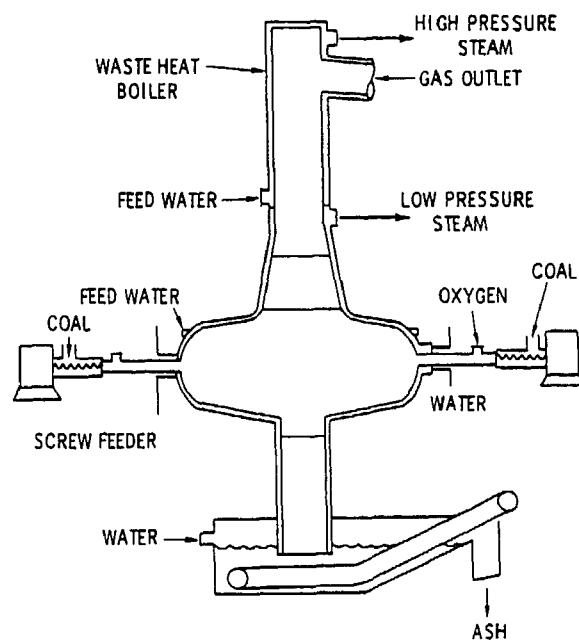
FIGURE 1. Koppers-Totzek Gasifier Schematic

TYPE OF FUEL	WESTERN COAL	EASTERN COAL	GREEN PETROLEUM COKE
GASIFIER FEED			
Dry Feed to Gasifier			
Analysis, Wt%			
C	72.7	69.9	88.0
H	5.3	4.9	4.5
N	1.1	1.3	1.4
S	1.0	1.1	4.3
O	9.0	7.1	1.0
Ash	8.9	13.7	0.2
Moisture	2.0	2.0	0.6
	100.00	100.00	100.00
Gross Heating Value of Dry Feed, Btu/Lb	13,135	12,640	15,690
Oxygen, Tons/Ton Dried Feed @ 98% Purity	0.878	0.849	0.950
Process Steam, Lb/Ton Dried Feed	814	810	1182
GASIFIER PRODUCTS			
Jacket Steam, Lb/Ton Dried Feed	600	554	629
High Pressure Steam, Lb/Ton Dried Feed @ 900°F/900 psig	2760	2675	3598
Raw Gas Analysis, Vol%, Dry			
CO	52.55	52.51	52.22
CO_2	10.00	10.00	10.00
H_2	36.09	35.96	35.40
N_2 + Argon	1.00	1.15	1.10
H_2S	0.34	0.36	1.20
COS	0.02	0.02	0.08
	100.00	100.00	100.00
Dry Gas Make - SCF/Ton Dried Feed	69,690	66,970	77,500
Gas Gross Heating Value, Btu/SCF, Dry	287	286	283
% Heating Value of Gas/Heating Value Feed (Gross Basis)	76.1	75.8	69.9

FROM COAL PULVERIZER

N_2 TO VENT

STEAM DRUM

SUPERHEATED STEAM

WASTE HEAT BOILER

SPRAY WATER FROM CLARIFIER

SERVICE BUNKER

ROTARY VALVE

FEED BIN

GASIFIER

O_2

STEAM

O_2 STEAM

SLAG QUENCH TANK

H_2O

BOILER FEED WATER

TO START-UP VENT

PRIMARY WASHER

SECONDARY WASHER

SLAG BIN

SLAG TO DISPOSAL

SLUICE WATER SURGE BIN

HIGH PRESSURE PUMP

FROM SLAG QUENCH TANK

CLARIFIER

SLUDGE TO DISPOSAL

MAKE-UP WATER

RAW GAS COOLER

TO SLAG QUENCH TANK

MAKE-UP TO SCRUBBING SYSTEM

HOT WELL

COLD WELL

COOLING TOWER

CONDENSATE (IF ANY)

COMPRESSOR

H_2S ABSORBER

DE-SULFURIZED GAS TO USERS

LEAN ABSORBENT

FOUL ABSORBENT TO STRIPPER

PUMP

FIGURE 2. K-T Gasification Process Schematic

oxygen into the gasifier through special metering heads or nozzles. The feed nozzles are arranged to inject the coal at velocities in excess of the flame propagation speed. The coal ash is completely liquefied in the flame zone, and about half of the ash in most coals drains from the bottom of the gasifier as molten slag into a quench tank. The remainder of the ash, which is entrained in the raw gas output, is generally solidified at the entry to the waste heat boiler beyond the gasifier by water spray injection to avoid ash adherence and build-up on the boiler surfaces.[4]

Problems have been encountered in some recent installations of atmospheric pressure Koppers-Totzek gasifiers due to the very low viscosity of the slag from certain feed coals at the 2200 K (3500°F) burner tip temperature. The Koppers-Totzek design depends on build-up slag on the ceramic lining of the reactors to protect the linings. Not only did such build-up not occur, due presumably to the very low viscosity of the slag, but there was apparently reaction and/or solution of the ceramic lining with the slag, resulting in rapid failure of the linings. Moreover, whereas about half of the slag from the lignite feeds (which are common to most of the sixteen Koppers-Totzek plants now operating around the world) would normally be expected to flow out of the bottom of the gasifier directly into an ash quencher, it was found that no more than about 5 to 10 percent of the slag could be recovered in this way. Most of the slag was going over into the waste heat boiler along with the gas, greatly overloading the ability of the design to handle the solidifying mixture.[4]

A partial solution to both of these problems has been to reduce the operating temperatures by increasing the steam-to oxygen ratio in the gasifiers. However, this has also decreased the carbon conversion efficiency to "somewhat below 90 percent."[4]

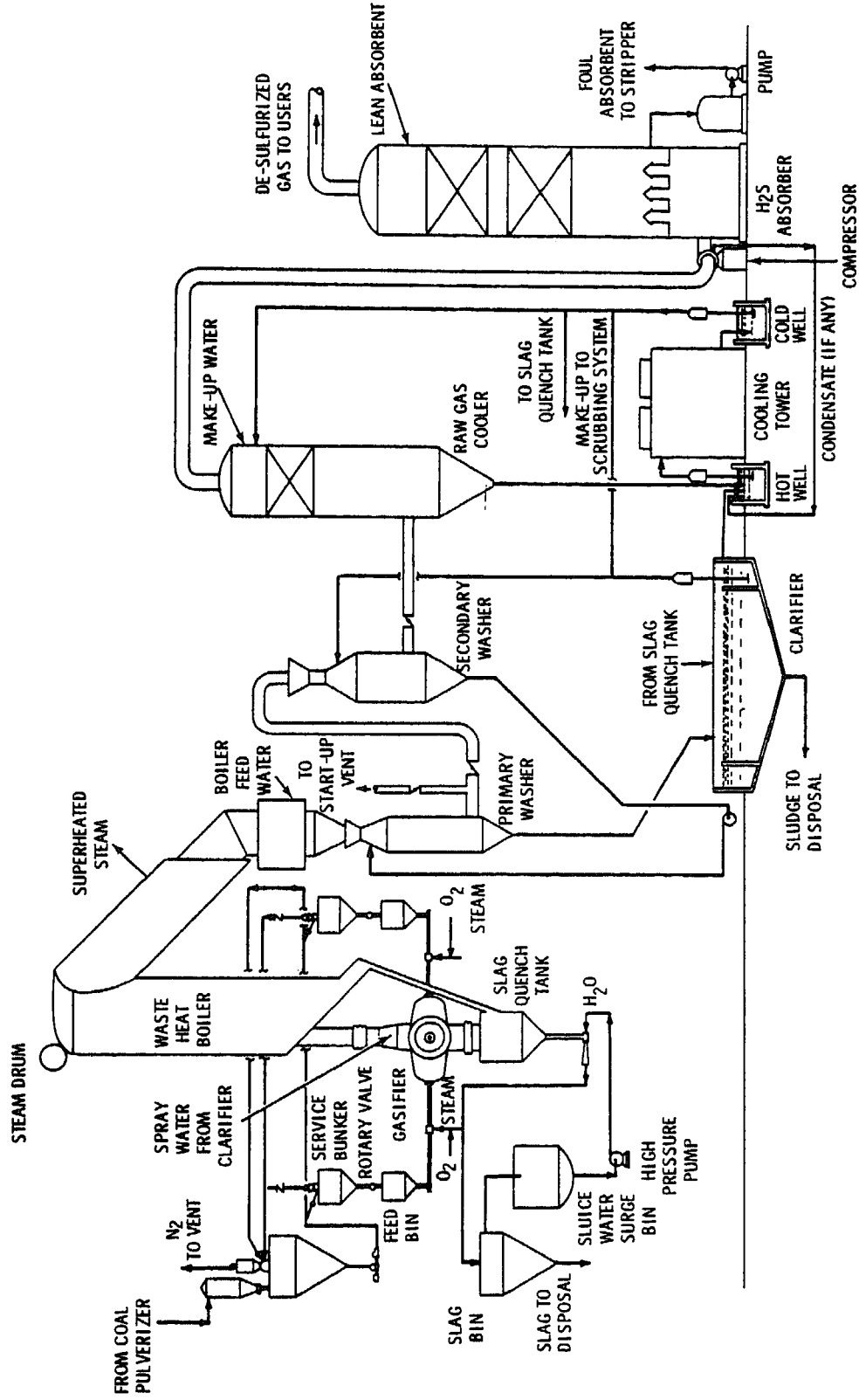Koppers (U.S.A.) indicates that they have developed designs for pressurized gasifiers operating at 60 psi and at 1000 psi and are seeking an underwriter for the construction of one or both of these systems. Presumably, only very small-scale reactors have actually been operated at these pressures. The primary stumbling block to pressurized operation has been the development of reliable coal feed devices.[4]

Koppers (U.S.A.)[4] has reported that Shell (Dutch) and Koppers (Germany) have operated a 5 t/d pilot unit near Amsterdam for over two years. The plant has operated successfully on all ranks of coals at a pressure of 450 psi, producing a gas whose composition consisted of about 95 volume percent CO plus H_2, 2.6% CO_2 and 0.3% CH_4.

A 150 t/d unit constructed in Hamburg combines the experience of Koppers in the entrained bed gasification of solids at atmospheric pressure with Shell's experience on high pressure partial oxidation of liquids. The plant, which is highly proprietary, is expected to start operation by September 1978.[a] Koppers (U.S.A.) is not involved in the development of the process, but expects to be able to license the process. They expect no commercial conclusion to be drawn with regards to the process before 1983

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a) Information received by telephone from Mr. James W. Bumbaugh, Koppers, Engineering and Construction Div., Koppers Company, Inc., Pittsburgh, PA, August 1978.

TEXACO COAL GASIFIER

The Texaco gasifier was developed by Texaco, Inc. at their Montebello Research Laboratory in California during the 1940's. It was routinely operated from 1946 through 1954 to provide synthesis gas for an on-site pilot plant that was a modification of the Fischer-Tropsch process.[5] Since 1953, the Texaco process has been in commercial use for the production of synthesis gas from petroleum feedstocks and is currently used in approximately 70 plants in over 20 countries.[6,7] The process, which was initially developed for the partial oxidation of natural gas, has developed the versatility to use light oils, residual oil, petroleum distillates, asphalt, heavy oils, or coal as feedstocks. The Texaco process is the only high pressure suspension gasification process that has been operated on an industrial scale. Most of this experience has been with heavy oil as feedstock and dates back to 1953.

The Texaco gasifier is a vertical cylindrical pressure vessel (up to 85 atm) with a carbon-steel shell, the top section where gasification occurs is refractory lined. The lower section (slag quench chamber), which contains a reservoir of water for the quenching of gas, is unlined steel.[6]

Process flow diagram of the Texaco coal gasification pilot plant is shown in Figure 3. In the process coal, which has been ground to pass through a 40-mesh screen, is mixed with water in a slurry mix tank. The resultant slurry containing about 40 to 60 wt.% coal is pumped through an optional preheater to a temperature of 700-1000°F or more. The coal particle size has been reported to be reduced further in this heating coil, either as a result of attrition or as a result of the rapid expansion of water undergoing evaporation.[5] Since the proportion of water required to slurry and pump the coal was greater than that required for efficient gasification, up to 75 percent of the steam is separated in a cyclone in front of the gasifier.

The coal feed slurry enters the reactor either axially at the top or tangentially near the top through a water-cooled burner nozzle of proprietary design. Preheated oxygen is fed through a separate water-cooled nozzle oriented to prevent impingement of oxygen on the wall of the reactor.[8] Slag flows through a constricted opening at the bottom of the reactor into a quench tank and becomes granulated. The granulated slag, which is heavier than water and which generally contains less than one percent carbon by weight, is removed periodically from the bottom of the quench chamber by a lockhopper system. The fine solids, or soot, which are lighter than slag and which are principally ungasified carbon, are continuously removed from the quench section as an aqueous slurry. These solids are concentrated in a settling system and may be returned to the slurry preparation system if desired. Since the settling system operates at near-atmospheric pressure, flash gases are evolved with pressure letdown. The gases are reportedly very similar in composition to the product gas, except for a higher percentage of CO_2 and H_2S.[5] If the clarified water from the settling system is recycled to the quench chamber and scrubbing section, a blowdown stream is required to maintain the total dissolved solids at a desired level.[5] This stream reportedly contains no tars or phenols. The quenched product gas can be treated in an acid gas removal system.

FIGURE 3. Texaco Pilot Plant Process Flow Diagram

1 COAL
2 WATER
3 OXYGEN
4 FUEL
5 AIR

6 MAKE-UP WATER
7 RAW PRODUCT GAS
8 GAS QUENCHING LIQUOR AND PROCESS
   CONDENSATE (SOOT WATER)
9 PRODUCT GAS CONDENSATE

10 CLARIFIED WATER
11 CLARIFIED RECYCLE WATER
12 QUENCHED PRODUCT GAS
13 FLASH GAS TO FLARE
14 VENT GAS FROM SLURRY THICKENER

15 PREHEATER FLUE GASES
16 STEAM (SLURRY PURGE)
17 SLAG FILTRATE BLOWDOWN
18 DEWATERED SLAG
19 SOOT WATER SLUDGE (FINE SLAG)

pressure steam, Texaco plans to incorporate a gas cooler in the pilot plant so that its performance can be studied.[9]

The pilot Texaco gasifier at Montebello operates at pressures up to 350 psig and has a reaction volume of about two cubic feet. The temperature in the reaction zone ranges from 2000 to 2500°F. Throughputs of 1000 lb/hr of coal have been reported. Carbon conversions are primarily controlled by the amount of oxidant fed to the system, and are typically above 90 percent on a single pass basis. Only limited performance data have been reported[10] with carbon conversions between 90 to 98%, thermal efficiency ranging from 75 to 80% and oxygen requirements of 350 to 375 scf/Mcf of make gas. The gas contained about 8% CO_2, 1% CH_4, and had a H_2/CO ratio of about one. It has also been reported that, the oxygen consumption rates ultimately expected are 15,000 to 20,000 scf per ton of dry coal with 80 to 90% of the heating value of the coal appearing in the form of hydrogen and carbon monoxide in the synthesis gas.

Very limited operating details and results using coal have been published for the Texaco process. Table 2 lists some typical results for gas, fuel oil, and coal firing.[5] It should be noted that at least for fuel oil operations the distribution of sulfur compounds in the product gas was very similar to that calculated for equilibrium. As an example, Texaco cited a study in which the observed sulfur distribution as hydrogen sulfide, carbonyl sulfide, and carbon disulfide was 89, 11, and 0.03 percent, respectively; and the calculated equilibrium distribution was 93, 7, and 0.05 percent, respectively.[11]

COMMERCIAL CONTROL SYSTEMS

The gasification of coal in an entrained flow system involves a number of processing steps. The steps in the direct process include coal storage, coal preparation, gasification, gas quenching, particulate removal and acid-gas removal. End use of the gas will determine if further gas processing, such as shift conversion, is required. In addition to the steps in the direct process, auxiliary facilities are required and usually include an oxygen plant, a sulfur plant, a utility boiler, raw water and waste water treatment facilities, and cooling towers.

The complexity of the multi-step process for coal gasification increases the difficulty of controlling environmental pollutants. All aspects of the conversion process, from coal storage to final product, require extensive study to assess the potential for pollutant emissions, determine actual emissions, and proceed to a control strategy which is technically and economically effective.

Figure 4 presents a simplified schematic of the overall process and delineates possible effluents from each processing step, excluding the mining operation. Each operation involved in the conversion process, from coal storage through final gas utilization, is a potential source of environmental pollution. Effluents from auxiliary facilities should also be considered.

The following discussion relates to the operations that are somewhat unique to an entrained flow gasification process. Operations such as coal storage, coal preparation, oxygen production, and the utility boiler are

| Fuel Type Fuel Composition, Wt.%	Natural Gas	Fuel Oil	Pittsburgh Coal	Japanese Coal
C	74.42	85.59	77.3	64.3
H	21.94	11.38	5.3	4.9
O	1.67	0.35	5.2	15.0
N	1.98	0.72	1.4	0.9
S	-	1.96	2.5	1.8
Ash	-	-	7.1	13.1
Moisture	-	-	1.2	-
Fuel Rate, lb/hr	1714	429	-	-
Oxygen/Fuel, lb/lb	1.30	1.02	0.84	0.66
Steam/Fuel, lb/lb	-	0.38	0.70	0.67
Gas Composition, Mole % (dry)				
CO	38.02	47.97	46.6	45.7
CO_2	2.19	3.65	11.5	13.2
H_2	59.54	47.45	38.7	37.9
CH_4	-	0.44	0.7	0.6
N_2	0.15	0.22	2.0	1.7
H_2S	-	0.02	-	-
COS	-	0.02	-	-
Gas Yield, scf(dry)/lb fuel	58.38	50.36	38.31	31.06
Materials per 1000 scf ($CO + H_2$)				
Fuel, lb	17.6	20.8	30.6	38.5
Oxygen, scf	271.7	252.3	306	302
Steam, lb	-	7.9	21.5	25.8
Carbon Conversion, %	100	96.6*	92.1*	91.3*

*Calculated from reported data
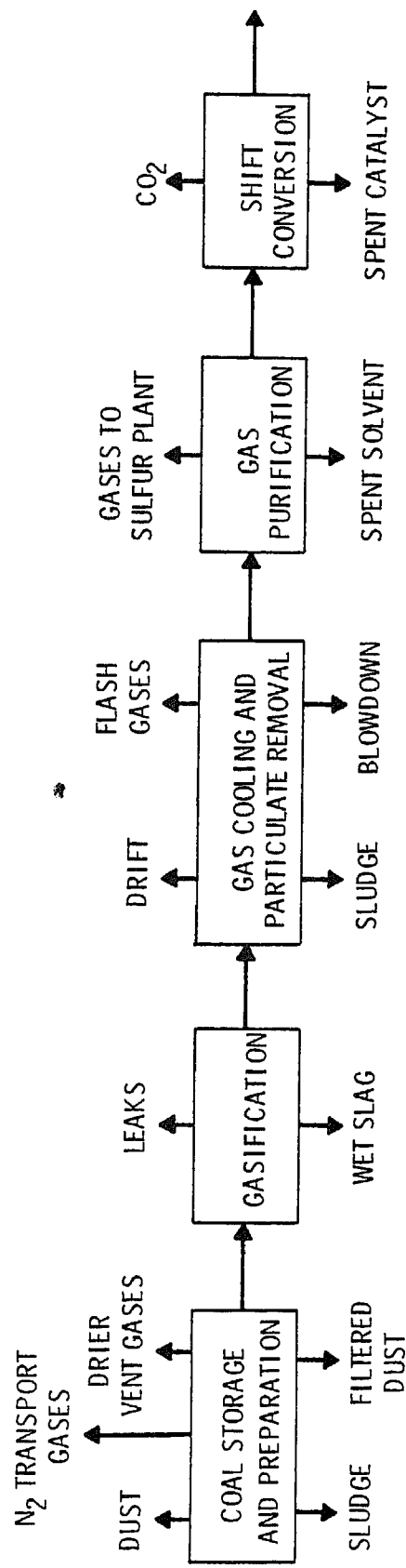
FIGURE 4. Effluent Streams From Coal Gasification

pressurized K-T and Texaco gasifiers.

GASIFIER OPERATIONS AND PARTICULATE REMOVAL

The objective of gasifier operations for the K-T and Texaco processes is to react coal with oxygen and steam to produce a synthesis gas consisting of H_2 and CO accompanied by varying amounts of CH_4. During gasification other gases are produced, including CO_2, N_2, H_2S, COS, and C_2H_6. Of these gases the sulfur compounds are of major consequence. Other potential pollutants may also be generated: tars, oils, phenols, ammonia, particulates, other organic material, and trace elements.

Although gaseous pollutants are produced in the gasifier, these are not of immediate environmental concern as they are contained in the raw gas leaving the gasifier and are treated in subsequent process treatment steps. Exceptions are emissions due to leaks in gasifier seals and in pressurized lock hoppers and other feeding systems. These leaks would allow gaseous pollutants to escape directly into the atmosphere and would be significant sources of pollution. This situation would require immediate correction.

Contaminated water streams appear to be the major potential source of pollution from the gasifier, gas cooling, and particulate removal systems. Solid residues in the form of ash, slag, soot and sludge will require land disposal. These solid residues will contain inorganic ashes, metals, and unreacted carbonaceous matter of unknown composition that may prove to be of consequence. At present most gasification schemes use mine backfill or landfill as the method of disposal for this material. This method of disposal may prove to be environmentally unsatisfactory for some wastes, especially ash residues that have a high potential for leachability. This problem can only be evaluated after complete analysis of specific gasifier waste streams.

Reaction zone temperatures in entrained flow gasifiers are necessarily high to achieve adequate conversion with a short residence time. Temperatures are in the range of 3300 to 3500°F in the K-T gasifier and 2000 to 2500°F in the Texaco gasifier. The product gas, therefore, contains no condensible hydrocarbons. No phenols, pyridines, or organics are produced. However, ammonia and cyanide are present in the K-T product gas. Gas analyses before and after particulate removal for a K-T system are shown in Table 3.[12] The analyses shown in Table 3 represent operating data from a plant using a primary and secondary venturi scrubber in which the gas is intimately contacted with recirculated water.

Discharges to Air

In the atmospheric pressure K-T system, discharges to the air could result from stripping the components dissolved in scrub water and direct contact cooling water by air in the cooling tower (see Figure 2). No further discharges to the air environment are foreseen since the product gas from particulate removal is compressed and passed to the acid gas removal system for further processing.

As shown in Table 3, some components are retained in the scrub water and cooling water.[12] All concentrations after particulate removal should increase by a factor of 1.3 over concentrations before removal because of the decrease in H_2O concentration resulting from condensation. Components retained in the scrub water are COS, HCN, SO_2 and NO. These could be stripped by direct contact cooling of the scrub water.

Component	Before Particulate Removal	After Particulate Removal
CO	37.36	49.50
CO_2	7.13	9.42
CH_4	0.08	0.11
H_2	25.17	33.35
N_2	0.30	0.40
H_2S	0.23	0.3
COS	178 ppmv	15 ppmv
HCN	288 ppmv	300 ppmv
NH_3	0.17	0.22
H_2O	29.19	6.20
Ar	0.32	0.42
SO_2	22 ppmv	15 ppmv
NO	7 ppmv	7 ppmv
Particulates (grains/scf)	11.57	0.002

In the Texaco system, possible contamination of the air environment could result from combustion of gases from the flash drum, see Figure 3. These gases are flashed from scrub water and quench water solutions after pressure letdown in the flash drum. These gases will probably have a composition similar to the product gas but richer in components such as CO_2, H_2S, COS, SO_2 and NO. This stream may require treatment before it can be flared.

Discharges to Water

In commercial K-T plants, the reduction in particulate concentration shown in Table 3 is accomplished in the washer cooler, venturi scrubbers and separator. About 50% of the ash content in the coal leaves the gasifier as a slag quenched in water at the base of the gasifier.

Water flow in the cooling and scrubbing system proposed for U.S. applications is shown in Figure 2. Solids retained in the water are removed in a clarifier. If water is not a premium consideration, a slurry can be pumped to a disposal area. Water conservation can be effected by filtering the slurry, returning the water to the circulating system, and disposing the filter cake by truck or railroad car transfer to the worked-out mine or disposal area. Since all the particulate matter is slagged in the gasification process, leachable contamination should be low. Water loss with the ash may serve as blowdown for the cooling towers.

Analyses of water from the various cleaning and cooling stages in the Kutahya, Turkey, plant are shown in Table 4.[12] This table shows the level of water contamination that occurs in commercial practice. Not all trace element concentrations are noted in Table 4; proposed drinking water standards, EPA 1975 limits, are 0.2 mg/l for cyanide.

TABLE 4. Process Water Analyses from Koppers-Totzek Gasification

Property	S	1	2	3	4	5	6
						Sample Location	
pH		8.8	8.8	8.9	7.5	8.8	8.8
Conductivity	S	7.6×10^{-4}	1.8×10^{-3}	2.0×10^{-3}	9.7×10^{-4}	1.8×10^{-3}	1.8×10^{-3}
CaO	mg/ℓ	78	101	78	85	135	179
MgO	mg/ℓ	97	161	194	102	145	113
Na	mg/ℓ	17.5	17.5	17.5	17.5	17.5	17.5
K	mg/ℓ	5.6	8.8	10	6.8	8.0	8.0
Zn	mg/ℓ	0.01	0.03	0.02	0.03	0.02	0.02
Fe	mg/ℓ	0.05	0.22	1.95	0.26	0.20	0.64
NH_4	mg/ℓ	0.32	157	184	25	137	122
NO_2	mg/ℓ	0.02	0.13	4.47	5.34	0.24	4.37
NO_3	mg/ℓ	58.2	3.32	13.7	34.0	24.7	22.9
PO_4 Total	mg/ℓ	1.89	0.81	1.21	1.69	0.81	2.70
Cl	mg/ℓ	18	85	96	53	57	46
SO_4	mg/ℓ	42	216	155	147	255	109
CN	mg/ℓ	0.26	0.52	12.5	7.0	1.4	14.0
H_2S	mg/ℓ				----------not detected----------		
$KMnO_4$ Consumed	mg/ℓ	8	9	400	14	11	145
COD	mg O_2/ℓ	14	18	128	18	16	63
SiO_2	mg/ℓ	14.8	16.0	14.8	30.6	19.8	42.6
Suspended Solids	mg/ℓ	14	4612	5184	278	3072	50
Cu	mg/ℓ	0.01	0.01	0.01	0.06	0.01	0.06

1) Cooling water to gasifier seal pot.
2) Water from gasifier seal pot.
3) Wash water after washer-cooler.
4) Wash water after Theisen washer.
5) Water into clarifier.
6) Water out of clarifier.
7) Water out of cooling tower.

necessitate control (cleanup or recycle) of the aqueous streams (such as scrubber cooling tower blowdown and drift loss) shown in Table 4. Drift loss from the scrubber cooling tower (16,220 lb/hr drift loss with coal feed rate of 562,500 lb/hr, 8,830 BTU/lb, from Reference 14) with the composition shown in Column 7 of Table 4 are included in Column 3 of Table 5 for comparison of releases to the standards even though drift losses are not a direct water discharge. Releases from drift loss approach the standards and indicate that water releases must be minimized, or waste water must be treated prior to release

It may be necessary to steam strip gaseous components such as NH_3, SO_2, and HCN from the clarifier water before it passes to the cooling tower to prevent their being stripped by direct contact with air. Koppers proposes to remove a bleed stream from the recirculated water system to a steam stripper. Gaseous NH_3, SO_2, and HCN flow to a Claus unit and are combusted while the stripped water is cooled and returned to the circulating system.

Considerations for the pressurized K-T and Texaco systems are similar to those for the K-T system. Water for gas cooling and scrubbing can be treated and recycled. Water streams from the Texaco process that must be treated include water from the slag quench chamber in the lower half of the gasifier unit, gas quenching liquor and process condensate, and clarifier water.

TABLE 5. Adjusted New Source Performance Standards
(pounds of pollutant per 10^{12} BTU feedstock, 30 day maximum)[a]

Pollutant	Petroleum Refineries	Coke Making	K-T Drift Loss Estimate
BOD	230-1015	477	200 (COD)
TSS	143-646	242	190
Ammonia (as N)	46-400	242	180
Oil and Grease	71-233	12	-
Phenols	1.5-7.1	5.8	-
Sulfide	1.2-5.8		

(a) Assumes heating values of 6.5 mm BTU/bbl of crude oil and 12,000 BTU/lb of coal, with a coke yield of 0.69 lb coke/lb coal.

system. Soot water, which contains dispersed soot and other suspended and dissolved matter, is drawn off near the bottom of the quench chamber and sent to a clarifier. No quantitative information is available on the characteristics of this stream; however, it is expected that the water will contain components such as shown in Table 4. Scrubber water (process gas condensate) from the scrubber knock-out pot is also sent to the clarifier. This stream is expected to contain suspended coal fines and slag, CN^-, $S^=$, ammonia, trace elements and organics.[15]

Water from the clarifier in the Texaco System is circulated to the flash drum where flash gas is vented to a flare. Make-up water is added to the clarified water in the flash drum and the water is recycled to the quench chamber.

Discharges to Land

Sludge from the clarifier and slag from the quench system for entrained flow gasifiers are usually sent to landfill. The sludge may be dewatered by filtration either before or after transport to a disposal site. Since all the solids have been slagged, very little leaching to ground water should result. The water associated with the slag and sludge will have the compositions shown in Table 4, columns 2 and 6 respectively.

Ash from the clarifier and slag quench system could have properties that significantly differ from power plant fly ash.[16,17,18,19] Ash from gasification processes is exposed to a reducing atmosphere, and elements may exist in a reduced form. Trace metals may be more soluble than fly ash trace elements in a number of water streams. This is likely to change effluent loadings to the waste water treatment facilities and, therefore, require alternative water treatment techniques. Furthermore, a change in solubility may affect the leachability of inorganic compounds present in the final slag to be disposed and runoff from disposal areas will have to be monitored until firm data is established. Koppers-Totzek has reported data on major components in some of their water streams (see Table 4), but no data are available on trace elements. No information on trace elements is available on slag quench, sluice, or elutriation waters. From the water analyses in Table 4 it is apparent that the ash from Kutahya plant would render the soil basic. Unlike mine refuse and coal preparation refuse, the residue from gasification does not contain sulfur (pyrite) which causes the acid mine drainage problem.

Discharges to land from entrained flow gasifiers is predicted not to cause any environmental problems. Since the ash has been slagged, dust problems from disposal sites should be minimal. Disposal sites should be monitored to characterize runoff streams.

ACID GAS REMOVAL

The removal of contaminants, especially sulfur, is a critical part of the gasification of coal. Contaminants that could potentially be present in the impure gas from entrained flow gasifiers consist of sulfur in the form of H_2S, COS, SO_2, and organic sulfur compounds, as well as nitrogen oxides, ammonia, cyanides, pyridines, hydrocarbons, odors, trace elements (Pb, Se, As, Te, F, Hg, Ga, Ge, Cd) that volatilize at gasification temperatures, and particulates. Gases from entrained flow systems are usually very low in hydrocarbons because of high reaction zone temperatures.

Purisol, and Selexol processes. These acid gas removal processes are capable
of reducing sulfur content in the gas to 0.1 ppm to 5 ppm. Carbon dioxide
is also selectively removed in these processes along with the sulfur gases.

    Other processes have been proposed for the removal of acid gases. One
of these is the Benfield Hot Carbonate Gas Purification process followed
by sponge iron and activated carbon traps, as proposed for the Synthane
process. Koppers-Totzek processes will use one of the three already men-
tioned processes, while proposed Lurgi gasification facilities will use
the Rectisol process or the Stretford process for H_2S removal.

    Commercial processes for removal of sulfur gases are listed in
Table 6.[20,21] These processes are usually insensitive to pressure, high
pressure operation being preferred. The efficiency of these processes for
removal of H_2S is dependent on the concentration in the gas to be treated,
but usually about 99% of the H_2S is removed. Regeneration of the solvent
is accomplished thermally or with steam. In the chemical solvent and
physical solvent processes, the H_2S stream from regeneration is usually sent
to a Claus plant where it is converted to elemental sulfur. In the direct
conversion and drybed processes, regeneration produces elemental sulfur
directly.

Discharges to Air

    Gas purification has several potential release areas. A scrubbing
system that uses a solvent must periodically dispose of spent solvent or
regenerate it in some manner; either alternative could cause environmental
problems. The extent of this disposal problem is dependent on the lifetime
of the solvent and characteristics of the contaminants. If the H_2S contain-
ing stream is not oxidized in a Claus plant, another problem may arise.
This problem involves traces of other components, such as NH_3, COS, or light
hydrocarbons, that may be present along with the H_2S. These compounds may
go through the sulfur production step unaffected, or may interfere with
the sulfur recovery process.

Discharges to Water

    Removal systems can be designed to reduce liquid effluents to zero pollu-
tants.[12] Purge streams are usually incinerated to eliminate discharges to
water. Alternatively, depleted solution may be sent to waste water treatment.

Discharges to Land

    No solid effluent streams are encountered in acid gas removal. Elemental
sulfur is produced in the Claus plant.

AUXILIARY FACILITIES

    Facilities not directly in the process flow include the oxygen plant,
sulfur plant, waste water treatment plant, makeup water treatment plant,
the cooling tower, and the utility boiler. Some of these auxiliaries are
needed to treat effluents from the main process.

    The auxiliary facilities represent well-developed technologies that
have been in commercial use for many years. In most cases, their application
to entrained flow gasification processes, such as the Texaco and K-T, is not
unique. Possible exceptions include the sulfur plant (Claus plant) and the
waste water treatment plant.

TABLE 6. Commercial Acid Gas Removal Processes

Process	Absorbent	Type of Absorbent	Temp. °F
Chemical Solvent type:			
MEA	Monoethanolamine	Aqueous solution	80 to 120
DEA	Diethanolamine	Aqueous solution	100 to 130
TEA	Triethanolamine	Aqueous solution	100 to 150
Alkazid	Potassium dimethylamino acetate	Aqueous solution	70 to 120
Benfield	Activated potassium carbonate solution	Aqueous solution	150 to 250
Catacarb	Activated potassium carbonate solution	Aqueous solution	150 to 250
Physical solvent type:			
Sulfinol	Sulfolane + Diisopropanomine	Organic solvent	80 to 120
Selexol	Polyethylene glycol ether	Organic solvent	20 to 80
Rectisol	Methanol	Organic solvent	<0
Direct Conversion:			
Stretford	Na_2CO_3 + anthraquinone sulfonic acid	Alkaline solution	
Drybed type:			
Iron Sponge	Hydrated Fe_2O_2	Fixed bed	70 to 100

to process stripped gases with a high CO_2 content relative to H_2S. Efficiency of sulfur recovery decreases as the inlet concentration of H_2S to a Claus plant decreases. An inlet concentration of over 20 volume % H_2S is desirable. The presence of CO_2 in high concentration can also present problems by reacting with H_2S to form COS. With the availability of Claus tail gas cleaning processes, adequate commercial technology for sulfur control is available for use with entrained flow systems. Sulfur recovery in the form of sulfuric acid and elemental sulfur is being practiced at K-T installations throughout the world.

Applicable commercial processing steps for waste water treatment include stripping for removal of dissolved gases (H_2S, NH_3, CO_2), clarification for removal of suspended solids, biological oxidation, and sand filtration. The main waste water sources are the slag quench water, particulate scrub water, and spent solvent solution. Waste waters from entrained flow systems will be low in dissolved organics since the high gasification temperatures destroy heavy organics. The low organic content should simplify waste water treatment.

ENERGY REQUIREMENTS

The environmental impact of an operation can be related directly to the energy used for that operation. It is, therefore, extremely important to determine the areas in a system that require large amounts of energy.

Energy requirements for different operations employed in the K-T gasification process were determined from literature sources and are tabulated in Table 7. Sources of information are referenced in the table.

<u>TABLE 7.</u> Process Energy Requirements

Operation	Required Energy, % of Gasifier Input Koppers-Totzek
Coal Preparation (drying and grinding)	6.3[a]
Particulate Removal	<1[b]
Compression	15.4[a] (7.2)[c]
Acid Gas Removal	4 - 7[d]
Oxygen Plant	11.1[e] (16.9)[a]
Sulfur Plant	--
Tail Gas Cleanup	0.1[f]
Cooling Water Pumps, Air Fans	1.8[a]

(a) Data from Reference 14, calculated as described above.
(b) Data from Reference 22, pp. 20-100 to 20-108.
(c) Adiabatic compression to 165 psig.
(d) Data from Reference 23.
(e) Data from Reference 20, p. 14.
(f) Data from Reference 24.

determined as equivalent fossil energy requirements, specifically, each pound of steam was considered to cost 1500 BTU of fossil energy and 10,000 BTU of fossil energy produced 1 kWh of electricity.

Generation of the oxygen required for coal gasification and gas compression are the major users of energy in the gasification systems. Coal preparation (mainly drying) and acid gas removal are also large users of energy. Examination of process improvements in these areas, therefore, have the greatest potential for energy savings. Decreasing energy demand will benefit the environment in direct proportion to energy savings. However, the areas represented as large energy users represent highly developed technology. It is unlikely, for example, that significant energy saving improvements in oxygen plant operation can be expected. Acid gas removal processes can be selected on the basis of their energy requirement, e.g. steam requirements for solvent regeneration vary significantly for different processes.[23]

CONCLUSIONS

Several conclusions may be drawn from this study:

1. Coal storage, preparation and drying processes are commercially available. Coal storage and handling methods used by coal-fired power plants should be directly applicable to gasification using Koppers-Totzek and Texaco gasifiers. Crushing and drying requirements for gasification are somewhat more severe than those encountered by coal-fired power plants.

2. Sulfur and particulates are completely removed from the product gas in the commercial operations as required for use of the gas for chemical synthesis. These systems have been in use for over 40 years. Claus plants are employed in some of these commercial operations to convert the sulfur compounds to environmentally acceptable elemental sulfur. Reduced H_2S concentration in stripped gases to the Claus plant will reduce efficiency for sulfur recovery.

3. Tail-gas cleanup processes for reduction of Claus plant emissions and increasing sulfur recovery are available.

4. Major energy users in the processes are oxygen production, acid gas removal, and gas compression.

5. Since essentially no tars or hydrocarbons are produced in entrained flow gasification processes, water cleanup problems are minimal and should cause no unique waste water treatment problems for conventional water treatment methodologies. Dissolved compounds such as NH_4, H_2S and HCN and leached trace elements are the contaminants of concern. Waste water will be cleaned and recycled for process use. Chronic loss of water results from direct contact cooling tower operation. Control of losses from evaporative cooling towers is a major concern.

6. Large quantities of ash and slag will be generated with commercial gasification processes. An assessment of ash compositions and ash disposal techniques should be undertaken to determine the adequacy of current control methodologies.

7. Although much information has been written about coal gasification processes, there are many areas in which data is lacking in the environmental aspects of the processes. These areas include: 1) determination of the fate of trace metals, especially those considered to be volatile and hazardous, 2) quantification of volatile emissions from cooling towers,

slag piles, 5) determination of volatile substances (H_2S, NH_3, and organics) from clarifiers and slag quench tanks, 6) determination of the chemical properties of clarifier effluent and sludge, and 7) a better general characterization of most process streams.

RECOMMENDATIONS

This study and previous studies reveal that, with the possible exception of trace elements, adequate control technology is commercially available. Improvements in these technologies are needed to reduce energy requirements and environmental releases. The major need is to demonstrate that the control systems give adequate cleanup with actual process streams. This can be done in two ways:

1. Characterize flows and control equipment performance in existing operating plants.
2. Install production capacity based on the gasification technologies and thoroughly characterize flows and environmental releases at these installations.

The first option involves getting permission from operating plants to instrument their facility to determine process flows and to monitor the area surrounding the plant. EPRI funded a study on gasification of COED char in a K-T gasifier at Puentes, Spain. The report on the results of this study has not been issued at this time. The fact that COED char was gasified in a K-T unit at Puentes, Spain, indicates that cooperation with operating plants and foreign countries is possible. However, operators are usually very sensitive concerning studies relating to environmental releases, and the flexibility in modifying or changing processing conditions would be severely limited in testing at a commercial facility.

Installation of production capacity based on these gasification technologies is the recommended approach. Rather than install units in a highly industrialized area such as Cedar Bayou, Texas, as recently announced,[25] it is recommended that units be installed where effects of trace elements and other releases can be thoroughly characterized.

The following steps are recommended to demonstrate the adequacy of environmental control technology for gasification:

*   Install a 300 t/d (or larger) ammonia fertilizer plant in a non-industrialized area.
*   Thoroughly characterize the state of the environment at the plant location before operations begin.
*   Monitor releases from the plant during operations. Determine all process flows in the operating plant.
*   Determine trace element behavior to see if any mechanisms for accumulation of toxic quantities are acting.

Successful demonstration of the project in an industrially undeveloped area would answer questions of environmental concern. Results would be extremely valuable in establishing environmental standards. This would allow employment of a technology to use coal to produce a product that is presently a large consumer of dwindling supplies of natural gas.

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Coal conversion processes employing wet cleaning of gases transfer a major fraction of coal chlorides and fluorides to the gas condensate. The presence of halides and other strong electrolytes, absorbed from the gas or leached from particulates, compromises the prospects for reuse of the condensate.

Preliminary absorption of halides involves a controlled two stage quench that collects particulates and absorbs strong electrolytes in a segregated, low volume, primary condensate. The larger volume secondary condensate collected from the second stage quench is amenable to partial desalination by steam stripping of volatile weak electrolytes and biological treatment for removal of organic compounds.

A study was made to assess the technical and economic feasibility of two stage gas quenching at a hypothetical producer gas plant operating on alternate feeds of high halide Eastern coal and low halide Western coal. The results indicated that a first stage quench collecting 10 percent of the total condensate would absorb over 99 percent of gas chlorides and over 97 percent of gas fluorides. Some thiocyanate was presumed to collect in the secondary condensate that compromised the efficiency of weak electrolyte removal by steam stripping and biotreatment. The ratio of electrolyte concentration for treated primary condensate to treated secondary condensate for Eastern and Western coals was 89 to 1 and 18 to 1 respectively. Comparative cost estimates of two-stage quenching versus single stage quenching with desalination of effluent by reverse osmosis indicated that two-stage quenching was more economical for high halide Eastern coal and that reverse osmosis was more economical for low halide Western coal.

It was concluded that the two stage quench system was economically favored as compared to reverse osmosis desalination of single stage condensate where the gasifier gas contains high halide content and/or high moisture content. The two-stage concept is considered to be widely applicable to coal conversion processes employing wet gas cleaning.

The mechanism and location of thiocyanate formation in two-stage quenching was not defined in the study. If thiocyanate forms during the first stage quench it is purged with the high electrolyte discharge. If thiocyanate forms during the second stage quench it will add to the electrolyte content of the secondary condensate that is reused in the process. Research is indicated to resolve the thiocyanate question as well as to any special materials requirements for the first stage quench system.

Coal conversion processes employing wet cleaning of gases transfer a major fraction of coal chlorides and fluorides to the wastewater discharge. The presence of halides and other strong electrolytes in wastewater compromises the prospects for reuse, unless resort is made to energy intensive desalination technology.

An alternate concept to desalination involves the application of a two-stage gas quench where the first stage preferentially absorbs strong electrolytes in a low volume flow and the second stage comprising most of the condensate is collected relatively free of strong electrolytes. Thus the preliminary absorption of halides and other strong electrolytes in a low-volume first stage quench produces a condensate from the second stage quench that is relatively free of strong electrolytes. The volatile weak electrolytes present in secondary condensates can be stripped from the water and the organic substances can be removed by bio-oxidation to yield an effluent that has a low dissolved solids content.

The purpose of the present study was the evaluation of the theoretical performance and economic feasibility of the two-stage gas quenching concept for a fixed bed coal gasification facility using 1500 tons per day of coal. The study compares the relative cost of two-stage quenching with single stage quenching plus equivalent desalination. The study examined both air blown and oxygen blown gasification technology, with air blown results selected for presentation herein. The analysis of performance is considered to be representative of tar producing coal gasification technology employing wet cleaning of producer gas. The analysis of practicality applies only to the system studied.

PROCESS DESCRIPTION

The hypothetical gasification plant selected for the study employed five 300 ton per day fixed bed gasifiers for an operational capacity of 1500 tons per day of coal. The gasifiers were modeled after the pressurized, stirred, fixed-bed gasifier of the Morgantown Energy Technology Center[1]. The gasifiers had an assumed diameter of 13 feet and were operated air blown at a pressure of 103 psia. Steam at a pressure of 110 psig and a temperature of 350° F was injected into the gasifier and the outlet gas temperature was estimated as 1050° F. The gasifiers were operated on Illinois No. 6 coal and Montana Rosebud coal with analyses as reported in Table 1. The Illinois No. 6 coal was selected as representative of a high halide Eastern coal. The Montana Rosebud coal was selected as representative of a low halide Western coal.

The gas from the hypothetical gasifiers was passed through a dry cyclone and a heat recovery system to yield a feed to alternative gas cleaning systems at a temperature of 400° F and a pressure of 95 psia. The first system illustrated in Figure 1 provided conventional single stage gas cleaning consisting of a venturi scrubber, a spray cooler and an electrostatic precipitator to produce a cooled gas at 110°F. The second system illustrated in Figure 2 provided two-stage gas cleaning consisting of a venturi scrubber followed by a sieve tray absorber in the first stage and a spray cooler

	Ill. No. 6 Coal	Montana Rosebud Coal
	wt%	wt%
C	65.70	50.56
H	4.80	3.18
S	3.70	1.09
N	1.10	0.90
O	8.04	9.81
Cl	0.25	0.03
F	120ppmw	30ppmw
Ash	11.20	9.73
H_2O	5.20	24.70
	100.00	100.00
Higher Heating Value, Btu/lb	11,750	8,611
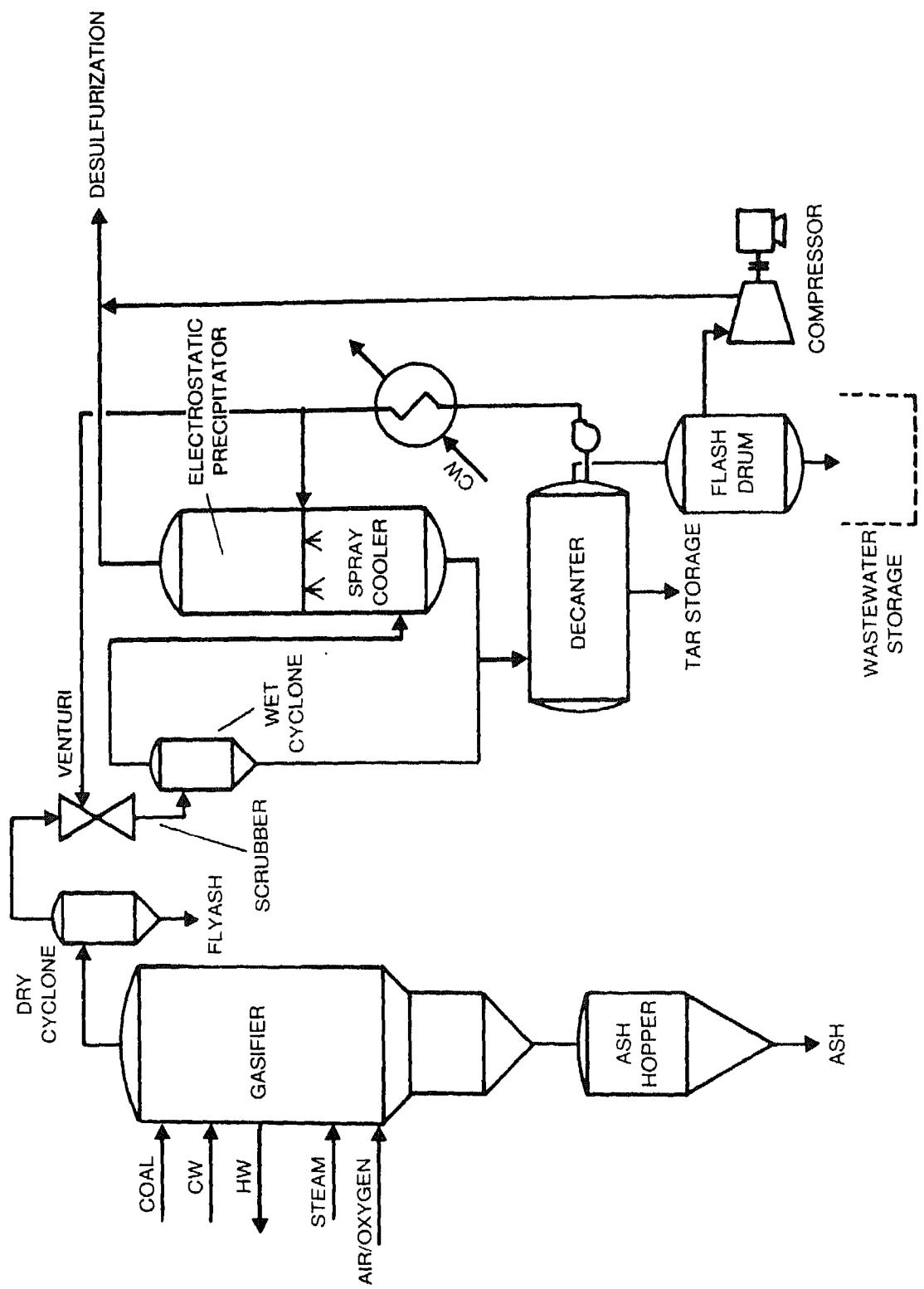
FIGURE 1: ILLUSTRATION OF PRODUCER GAS CLEANING BY SINGLE STAGE QUENCH

FIGURE 2: ILLUSTRATION OF GAS CLEANING BY TWO STAGE QUENCH

from 5 to 30 percent of the moisture in the trouble gave over the gas. The condensation was controlled by operation of the first stage decanter on a variable level basis in conjunction with a controlled blowdown from the system. The selected blowdown rate was proportioned to the air feed rate to the gasifier. The temperature of the quench liquid was controlled by the level in the decanter so as to condense more water as the level in the decanter dropped.

Concepts for treatment of condensates collected from single stage and two-stage quenching are illustrated in Figures 3 and 4. The condensates discharged from the gasification process were stripped with steam for removal of NH3 and H2S, which were returned to the gas prior to desulfurization. Separate strippers were required for first stage and for second stage condensates. Sodium hydroxide was added to strippers operating on single stage and first stage condensates to free fixed ammonia. The addition of sodium hydroxide was not required for the stripping of second stage condensates.

The bottoms from the strippers were biologically treated by the activated sludge process for removal of cyanides, thiocyanates, phenols and other organics. The effluent was filtered by granular media filtration for capture of fugitive suspended solids. Separate treatment facilities were required for condensates from first and second stage quenching.

METHODS

The study involved the conceptual design of process units, estimates of process performance and estimates of costs. The gas composition from the coal feeds given in Table 1 were estimated from material and energy balances keyed to operational data obtained from the MERC pilot plant stirred, fixed bed gasifier with heat losses taken as 2 percent of the total heat input. Where supplemental information was required for the analysis, performance projections were keyed to operating data from the Lurgi fixed bed gasifier at Westfield Scotland (2).

The chemical characteristics of the condensates were estimated with the assumption that equilibrium conditions were achieved in the absorption tower and in the spray cooler for the overhead temperature and pressure of each device. That is, the condensate blowdown was assumed to be in equilibrium with the vapor leaving the towers. Chemical equilibria were estimated by methodology of Edwards et. al. (3) supplemented by empirical correlations based on operational performance of similar systems.

The computer program (WAVES) developed in the reference predicts vapor liquid equilibirum for the system NH_3 - H_2S - HCN - SO_2 - H_2O. The program was modified to predict vapor liquid equilibirum for the system NH_3 - CO_2 - H_2S - HCN - HCl - HF - H_2O and applied to the prediction of condensate characteristics. The condensate characteristics predicted by the program were adjusted to include absorption of phenol, the presence of tar and the formation of thiocyanate. Thiocyanate formation is a complex phenomenon that was not resolved in the study. Based on coke plant correlations it was assumed that approximately 70 percent of the cyanide absorbed was converted to thiocyanate in the usual case where excess sulfur was present in the system.

FROM GASIFIER

HEAT RECOVERY

QUENCH & COOL

ELECTROSTATIC PRECIPITATOR

CLEANED GAS TO DESULFURIZATION

TAR & CONDENSATE

DECANT & STRIP

NH3 + H2S + HCN

TAR

BIOTREAT & FILTER

SLUDGE

DESALINATE

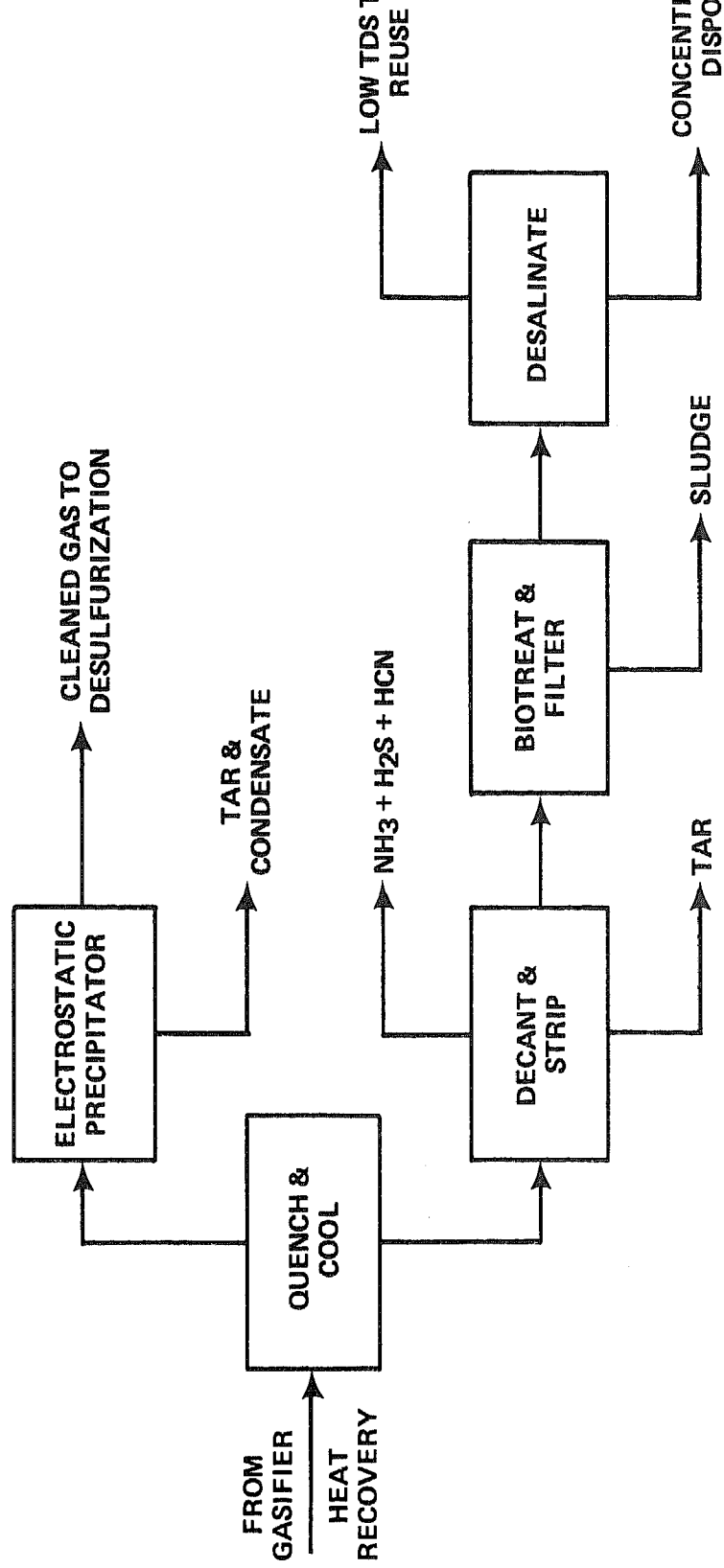LOW TDS TO REUSE

CONCENTRATE DISPOSAL

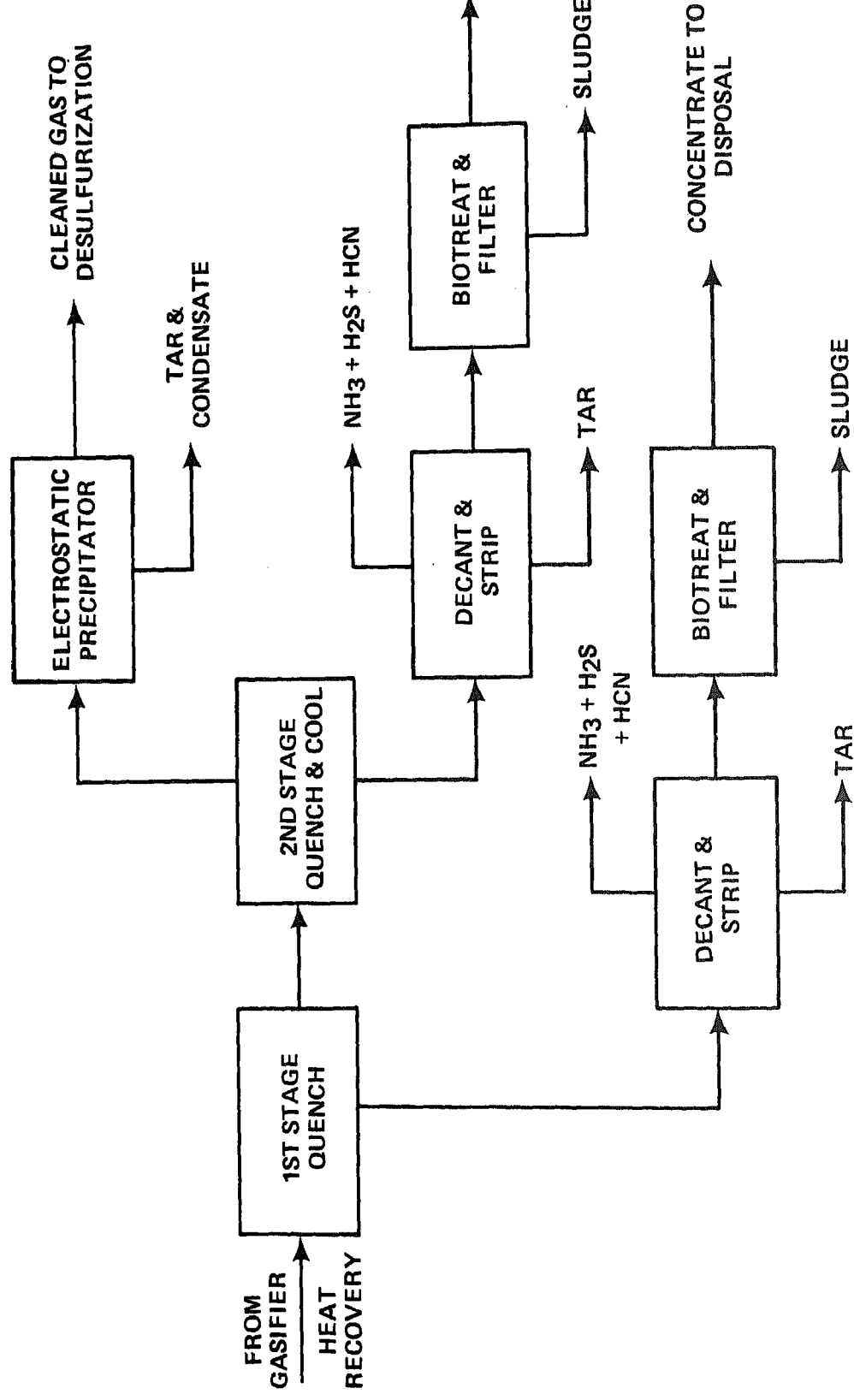FIGURE 3: CONVENTIONAL GAS CLEANING AND CONDENSATE TREATMENT

FIGURE 4: TWO STAGE GAS CLEANING AND CONDENSATE TREATMENT

residuals in the stripper bottoms of 50 mg/l of NH_3 and 5 mg/l of H_2S. Estimates of residual concentrations in the stripper bottoms were based on analysis of vapor-liquid equilibria adjusted by performance correlations from coke byproduct plants and petroleum refineries (4)(5). Based on performance correlations, the phenol residual in the stripper bottoms was estimated as 80 percent and total cyanide residual was estimated as 60 percent of input values.

The activated sludge facilities consisted of equalization, aeration, settling, granular media effluent filtration and attendant sludge dewatering systems. The systems were designed to operate in a temperature range of from 75 to 95° F at a sludge loading of 0.05 lbs. phenol per lb. mixed liquor volatile suspended solids. The performance of the systems was estimated from correlations with waste treatment results at coke plants and gasification plants.

Order of magnitude estimates were prepared to enable comparison of costs of conventional single stage quenching with costs of two-stage quenching. The estimates were prepared from engineering flow sketches and sized equipment lists. The scope of the estimates encompassed the gas cleaning trains, wastewater storage facilities, wastewater stripper facilities and wastewater treatment facilities. Order of magnitude estimates were also prepared for wastewater desalination by reverse osmosis.

RESULTS

The higher halide and sulfur contents of the selected Illinois No. 6 coal described in Table 1 as compared to the selected Montana Rosebud coal yielded higher concentrations of HCl and HF in the gasifier raw gas as indicated in Table 2. Residual concentrations of HCl and HF in the cooled gas leaving the gas train were less than 0.0001 percent of gasifier gas concentrations. Thus halides were projected to be substantially removed by effective wet gas cleaning. For a given coal, the cooled gas leaving the electrostatic precipitator had essentially the same composition whether processed by single stage or two-stage quenching.

Figure 5 illustrates the predicted relationship for HCl absorption as a function of the water condensed in the first stage quench. The combination of the venturi scrubber (15 in wg. pressure drop) plus the sieve tray absorber with 9 trays was indicated to remove 99.9999 percent of the chlorides from Illinois No. 6 producer gas at a condensation level of 20 gallons per ton of coal fed. This constituted essentially complete removal of chlorides in the first 20 gallons (7 percent) of a total of 290 gallons of condensate produced per ton of coal fed. Somewhat higher absorption of HCl was projected for operation with Montana Rosebud due to increased alkalinity of the condensate.

The predicted removal of HF as a function of volume of condensate is presented as Figure 6. With producer gas from Illinois No. 6 it was projected that a first stage quench of 30 gallons per ton would absorb over 98 percent of the HF from the gas. This amounted to 98 percent removal of fluoride in the first 10 percent of the total condensate. Fluoride removal from gas produced from Montana Rosebud was predicted to be higher because of increased alkalinity in the condensate. Thus the concept of preliminary absorption of halides was theoretically viable.

The projected results of steam stripping and biotreatment of condensates

|	Illinois No. 6 Mole %	Montana Rosebud Mole %
CO_2	9.56	11.72
CO	9.90	11.88
H_2	15.01	16.32
H_2O	30.73	21.23
CH_4	1.59	1.69
C_2H_6	0.14	0.17
$H_2S + COS$	0.47	0.22
$N_2 + A$	32.38	36.47
NH_3	0.17	0.27
HCl	311ppmv	60ppmv
HF	28ppmv	11ppmv
HCN	173ppmv	272ppmv
	100.00	100.00
Higher Heating Value, Btu/scF	102.9	114.0
Gas outlet temperature ^{o}F	1050	1050
Operating Pressure Psia	103	103
Gas Flow SCFM	178,800	112,100

CHLORIDES REMAINING IN GAS AFTER FIRST STAGE QUENCH
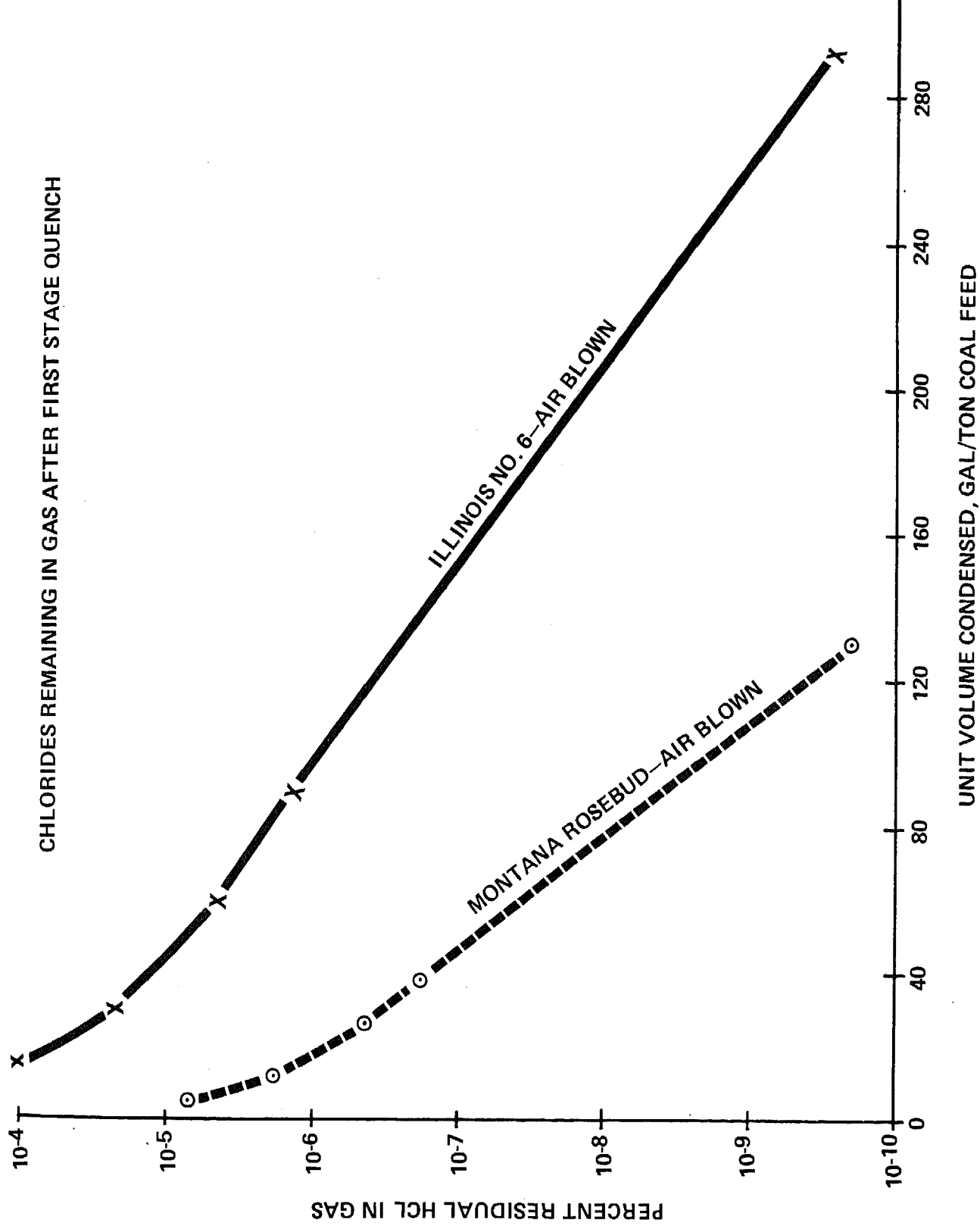
FIGURE 5: EFFECT OF UNIT VOLUME CONDENSED ON ABSORPTION OF CHLORIDES

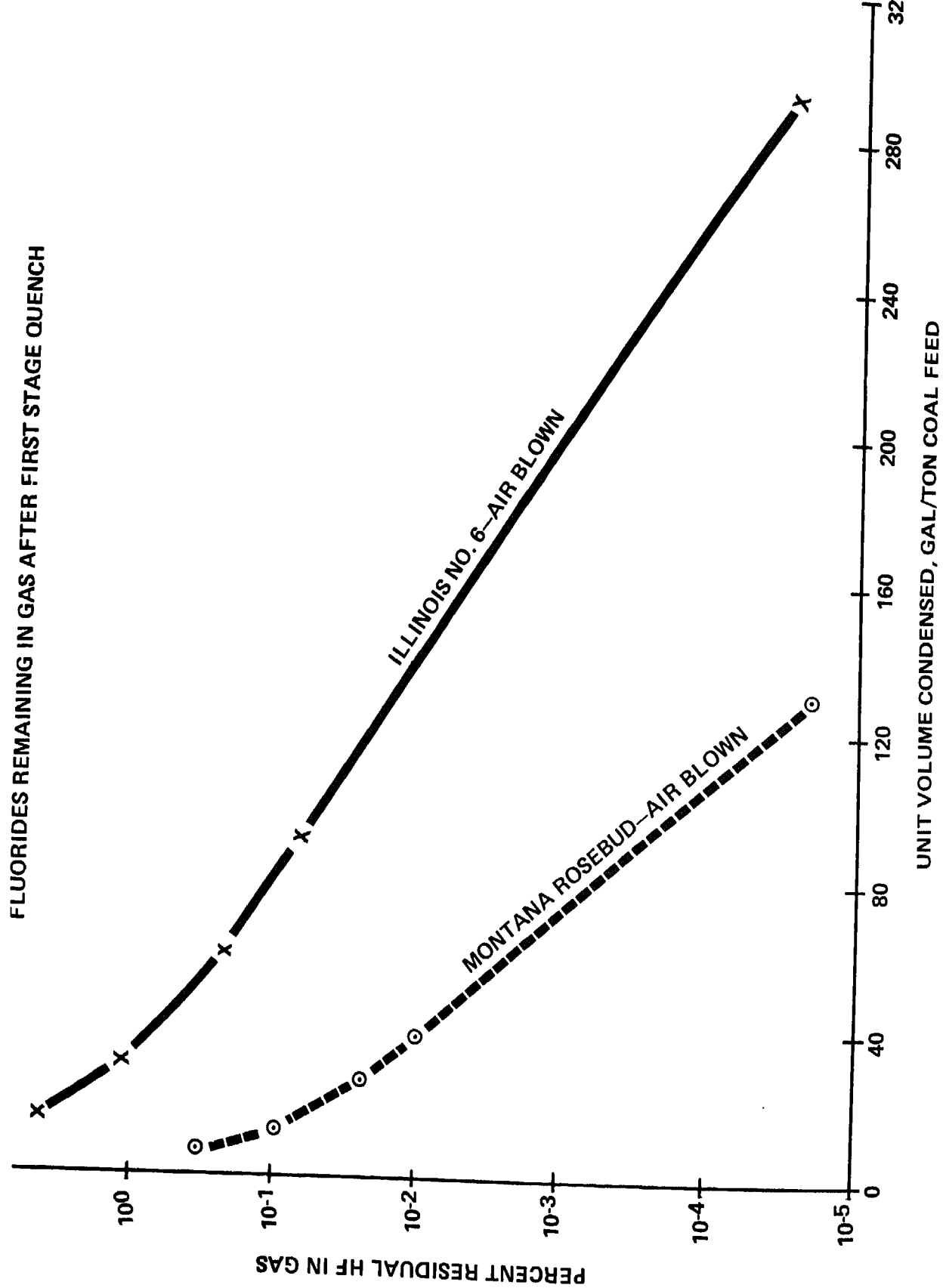FIGURE 6: EFFECT OF UNIT VOLUME CONDENSED ON ABSORPTION OF FLUORIDES

Steam stripping was indicated to effectively remove volatile weak electrolytes such as NH_3, CO_2 and H_2S. Free cyanide would also be quantitatively removed but it forms stable complexes of low volatility with metals such as iron and it reacts through various mechanisms with sulfur compounds during cooling of the gas to form thiocyanate - a strong electrolyte. Thiocyanate and metal cyanide complexes are refractory to the steam stripping process and therefore go with the stripper bottoms to biological treatment.

Biological treatment is projected to achieve excellent conversion of phenol plus substantial conversion of other organics and thiocyanates. The degradation of thiocyanate to ammonia and sulfate will contribute unwanted electrolyte to the second stage quench. The analysis projected that the strong electrolyte content of the second stage quench was 9 percent of a single quench and 1.1 percent of the first stage quench of 34 gallons per ton Illinois No. 6 coal feed. Thus the condensate from the second stage quench was of better quality for reuse than the condensate from the single quench.

The predicted results of steam stripping and biotreatment of condensates from gasifier operation on Montana Rosebud coal are presented in Table 4. The predictions forecast excellent removal of volatile weak electrolytes in the stripper and excellent removal of phenol by biological treatment. The strong electrolyte content of the second stage condensate was projected as 34 precent of the single quench condensate and 5.4 percent of the first stage condensate of 13.8 gallons per ton coal feed. The lower relative performance indicated for two-stage quench systems on Montana Rosebud was attributed to the lower halide content of the coal feed.

A cost comparison of single stage and two stage quench systems is facilitated by reference to Figures 3 and 4. The single stage quench will require a desalination operation to produce low electrolyte water for reuse whereas the two stage quench entailed the inclusion of a sieve tray absorber in the first stage quench and independent facilities for decanting, stripping and biotreatment of the first stage condensate.

Table 5 presents a comparison of estimated capital cost differences for the hypothetical gasifiers designed for air blown operation on Illinois No. 6 and Montana Rosebud coals. The capital cost for gas cleaning and condensate treatment systems was higher for two stage quenching than for single stage quenching. The difference was estimated as 2.2 million dollars for operation on Illinois Number 6 and 2.3 million dollars for operation on Montana Rosebud. The upgrading of single quench wastewater quality from Illinois No. 6 by application of reverse osmosis to attain comparability with the two stage quench was indicated to be cost ineffective. With Montana Rosebud the capital cost estimates indicated that there was potential for upgrading single quench water quality or for disposal to pond evaporation. Pond evaporation of single quench would feature a loss of the value of the second stage quench as makeup to reuse circuits. Pond evaporation was not evaluated for Illinois No. 6 operation inasmuch as it is not a viable alternative for the Eastern U.S.

A comparison of estimated annual costs is given in Table 6 for single stage and two stage quench systems with equalized reuse potential. Equalized reuse potential is taken as the separation of a reverse osmosis concentrate

Table 3: Effect of Treatment on Condensate Characteristics
Illinois No. 6 - Air Blown

Component	Raw Condensate			Condensate After Stripping			Biotreated Condensate		
	Single Quench	10% Quench	Final Quench	Single Quench	10% Quench	Final Quench	Single Quench	10% Quench	Final Quench
H_2O gal/ton coal	292	30.1	262	293	33	261	294	34	259
NH_3, mg/l	5310	10880	4671	50	52	50	44	24	42
CO_2, mg/l	10740	360	11790	5	5	5	0.1	0.1	0.1
H_2S, mg/l	350	44	63	5	5	5	-	-	-
HCl, mg/l	2110	20480	<1	-	-	<1	-	-	-
HF, mg/l	104	1000	1.3	-	-	1.3	-	-	-
CN, mg/l	50	0.61	51	15	0.15	15	3.0	0.2	3.0
SCN, mg/l	260	3.2	275	171	1.9	177	10	2	10
Phenol, mg/l	3329	2209	3640	2640	1630	2920	0.1	0.1	0.1
pH	7.1	5.8	7.2	8-10	8-10	7-9	7.7	7.8	7.1
NaCl, mg/l	-	-	-	3460	29100	-	3380	29200	1
NaF, mg/l	-	-	-	230	1860	-	219	1870	2
SO_4, mg/l	-	-	-	-	-	-	282	14	291
TSS, mg/l							25	25	25
Total Equivalent Strong Electrolyte, mg/l as NaCl							4028	31800	359
Concentration Ratio							11.3	89	1.0

Table 4: Effect of Treatment on Condensate Characteristics
Montana Rosebud - Air Blown

Component	Raw Condensate			Condensate After Stripping			Biotreated Condensate		
	Single Quench	10% Quench	Final Quench	Single Quench	10% Quench	Final Quench	Single Quench	10% Quench	Final Quench
H_2O gal/ton	124	13.0	111	123	13.4	109	123	13.8	109
NH_3, mg/l	11990	4866	12730	50	51	50	40	4	31
CO_2, mg/l	27110	1888	29270	5	5	5	-	-	-
H_2S, mg/l	199	75	225	5	5	5	0.1	0.1	0.1
HCl, mg/l	601	5718	>1	-	-	>1	-	-	-
HF, mg/l	60	574	>1	-	-	0.07	-	-	-
CN, mg/l	78	3.2	80	24	0.93	24	4.8	0.7	4.8
SCN, mg/l	410	16	-	270	11	279	10	2	10
Phenol, mg/l	6299	4675	7239	5056	3637	5824	0.1	0.1	0.1
pH	7.5	6.8	7.6	8-10	8-10	7-9	7.5	7.6	7.1
$NaCl$, mg/l	-	-	-	966	8619	-	976	8702	1
NaF, mg/l	-	-	-	127	1134	-	128	1145	1
SO_4, mg/l	-	-	-	-	-	-	447	43	458
TSS, mg/l	-	-	-	-	-	-	25	25	25
Total Equivalent Strong Electrolyte, mg/l as NaCl							1649	10350	561
Concentration Ratio							2.94	18.4	1.0

Table 5

Estimated Capital Cost Differences for Single and Two Stage Quench Systems

	Illinois No. 6		Montana Rosebud	
	Single Quench MM$	*Two Stage Quench MM$	Single Quench MM$	*Two Stage Quench MM$
1. Gas Cleaning & Cooling	8.40	9.50	4.00	5.50
2. Condensate Stripping & Biotreatment	7.20	8.30	5.50	6.30
Sum of 1 & 2	15.60	17.80	9.50	11.80
3. Two Stage - Single Stage		+2.20		+2.30
Difference with Effluent Equalized by:				
4. Reverse Osmosis	+0.50		0	+0.70
5. Pond Evaporation	NA	NA	0	0

*Condensate from first stage quench = 10% of input gas moisture

Table 6

Estimated Annual Cost Differences for Single Stage
and Two Stage Quench Systems with Equalized Reuse Potential

	Illinois No. 6		Montana Rosebud	
Cost Component	Single Quench $/yr	*Two Stage Quench $/yr	Single Quench $/yr	*Two Stage Quench $/yr
A. Quench & Condensate Treatment				
Operation @ 2.25 men		45,000		45,000
Maintenance @ 1.0% of Capital Cost		22,000		23,000
Miscl. LS		5,000		5,000
Capital Recovery @ 20%				140,000
B. Reverse Osmosis				
Operation & Maintenance	330,000		110,000	
Capital Recovery @ 20%	100,000			
Subtotal	430,000	72,000	110,000	213,000
Excess Annual Cost	358,000		103,000	

*Ten percent of gas moisture condensed in first stage.

The analysis in Table 7 indicates that the single quench system plus reverse osmosis operating on Illinois No. 6 coal is more expensive by about 360,000 dollars per year than a two stage quench system. The finding is considered characteristic of high halide coals.

With Montana Rosebud coal, the analysis in Table 7 suggests that the two stage quench system is more expensive by about 100,000 dollars per year than the single quench system plus reverse osmosis. The finding is considered characteristic of low halide coals that yield a small volume of condensate.

DISCUSSION

The applicability of a gas cleaning system using a two stage quench to effect preliminary absorption of halides has been indicated to be technically feasible. The process objectives of capture of particulates, absorption of strong electrolyte gases and efficient demisting in the first stage quench were attainable by application of conventional process technology. The objective of control of the unit volume of first stage condensate was feasible by engineered application of a variable level first stage tar decanter. The analysis of benefits of the two stage quench are considered conservative inasmuch as the analysis was based primarily on absorption of HCl and HF. In actuality, the isolation of the secondary condensate from contact with flyash and volatilized salts would increase the contrast between the quality of primary and secondary condensates. The quality of the secondary condensate is expected to be far superior to the primary condensate. The combination of steam stripping and biotreatment of the condensate from the second stage quench is indicated to produce an effluent of low dissolved solids content. It is evident that the low dissolved solids effluent would be amenable to reuse as service water to the coal conversion process with substantially less upgrading. than comparably treated condensate from a single stage gas cleaning process. Parenthetically it should be recognized that activated sludge effluents from treatment of coal conversion wastes characteristically contain low concentrations of organic matter - including some dark color bodies, so supplementary treatment would be required for some reuse applications.

The formation of thiocyanate during two-stage quenching is an enigma that was not resolved in the study. Appreciable thiocyanate is usually present in condensates from single stage quenching of producer gas and coke oven gas. It is established that thiocyanate can form as a result of reaction of free cyanide with sulfur, organic sulfur or oxidized inorganic sulfur (6) (7) (8). The dilemma in two-stage quenching is the estimation of the extent of thiocyanate formation in the second stage quench.

In two-stage quenching, the first stage quench cooled the gas to the 230-280° F range depending on the specific situation. It can be speculated that thiocyanate formation may occur in the first stage inasmuch as oxidized sulfur would be absorbed, and particulates bearing free sulfur and possible catalytic properties would be removed. Thiocyanate formed in the first stage quench would be removed from the process with the high electrolyte purge and would not register as electrolyte in the condensate from the second stage quench.

Thiocyanate formation in the second stage quench would be favored by the presence of organic sulfur, ammonia and cyanide as well as by temperature conditions. The limited availability of oxidized sulfur or external oxidant would presumably restrict reaction between cyanide and sulfide. However, reactions

is believed that the thiocyanate concentrations assumed to exist in condensates from the second stage quench were sufficient to cover the situation. It is conceivable that lower concentrations would be realized in practice -- which would register as improved quality of second stage condensate.

Absorption of HCl and HF in the first stage quench was assured by installation of a sieve tray absorber in conjunction with the venturi scrubber. The sieve tray absorber was the principal gas train component in the cost differential between single stage and two-stage quenching. It follows that cost savings would be realized if the combination of venturi scrubber plus efficient mist eliminators could be experimentally verified as adequate from the standpoint of absorption. Absorption of HF was indicated to control the design of the absorption system. Efficient mist elimination between first stage and second stage quenches is essential.

The cost estimates were prepared on the basis of carbon steel vessels and tanks in the gas train. The high electrolyte concentration of condensate from first stage quench, combined with suppressed pH, could necessitate the application of special corrosion resistant materials. Consultation with chemicals industry design engineers produced the recommendation of titanium clad vessels and tanks. Consultation with coke byproduct plant design engineers produced the recommendation of carbon steel with the expectation that the units would be tar coated. The position of the author is that the materials situation warrants experimental investigation including the possible application of neutralization in conjunction with corrosion inhibitors. A requirement for exotic materials would compromise the cost analysis presented herein.

The applicability of biological treatment to the wastewater was assumed inasmuch as coke and gas house liquors have been biologically treated for over 40-years. However, it is also recognized that problems have been experienced with biological treatment of some coal conversion process wastes, especially when the electrolyte concentration was high (9). For study purposes it was assumed that treatment problems could be resolved by process modifications to suit the specific situation. Some reservation is also expressed regarding the applicability of reverse osmosis to substrates containing a variety of non-specific organic compounds. The record of the process is spotty for such applications, but some latitude is available by process modification.

CONCLUSIONS

The following conclusions were developed during the course of the study:

1. The concept of preliminary absorption of halides and other strong electrolytes in a low volume primary condensate was indicated to be technically feasible for the gasification system studied. The essential features of the first stage quench are particulate removal, strong acid gas absorption and mist elimination. The technology is considered to be widely applicable to coal conversion processes employing wet gas cleaning.

2. The two stage quench system was indicated to be economically favored as compared to reverse osmosis desalination of single stage condensate where the gasifier gas contains high halide content and/or high moisture content.

3. Thiocyanate in the secondary condensate was indicated as a possible limitation to water quality that was not quantified in the study.

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ENVIRONMENTAL CONTROL ACTIVITIES ON SLAGGING FIXED-BED GASIFICATION AT THE GRAND FORKS ENERGY TECHNOLOGY CENTER

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1. INTRODUCTION

Environmentally related studies of slagging fixed-bed gasification at the Grand Forks Energy Technology Center (GFETC) were initiated in 1976. A principal factor involved was the availability of a pilot-scale fixed-bed gasifier which could be quickly restored to operational status. Initially the pilot plant and gasifier was constructed and operated under the Bureau of Mines during the period 1958-1965 to demonstrate the feasibility of slagging operation and the parameters involved. The major objectives of the reactivated project are to develop: 1) a scaleable process data base on feed/ product material balance, and 2) a detailed environmental assessment of the slagging fixed-bed gasifier (SFBG) process. The pilot plant has been operated in its original configuration for two years, however, plant and gasifier capabilities will be significantly expanded by modifications which are currently in progress. When modifications are completed and operation resumed, information will be obtained on a variety of test coals, including both low-rank non-caking coals (lignites and subbituminous) and bituminous coals with a range of caking characteristics.

The environmental assessment will include extensive sampling and analyses of process streams to characterize gaseous, solid, and liquid effluents, and testing of pilot plant-scale simulations for treatment of liquid effluents to establish the feasibility of zero discharge of liquids and safe disposal of solid wastes. The objectives of the GFETC project directly support the application of the slagging fixed-bed gasification technology to commercial development. The 25 ton/day gasifier has, at present, the unique capability of generating coal-specific data at reasonable cost for the large number of candidate U.S. coals.

In the particular area of liquid effluents and their treatment, a major part of the assessment performed on the SFBG is believed to be substantially applicable to fixed-bed, dry-ash gasifiers proposed to be used in first generation SNG plants. This will be validated, if possible, through comparative tests or bench-scale simulations. The GFETC gasifier can then provide information desired by the public on specific feed coals proposed for dry-ash SNG projects and industrial applications.

2. DESCRIPTION OF PILOT PLANT FACILITIES

The gasifier at the Grand Forks Energy Technology Center is a pilot-scale version of a conventional pressurized fixed-bed gasifier. In the commercial "dry-ash" process, gasification temperatures are maintained sufficiently low by the use of excess steam to allow removal of the ash in

as a molten slag. Two important advantages are obtained in slagging compared
to dry-ash removal operation. The steam consumption per unit of coal gasified
in a slagging gasifier is about one-fourth of that required for a dry-ash
unit, while at the same time, the gas production capacity per unit cross-
sectional area is as much as three or four times that of the dry-ash gasifier.

Figure 1 is a cross-sectional view of the original GFETC gasifier. Coal
is batch-charged to a lock hopper and gravity feeds into the main body of
the gasifier. The coal is heated by the countercurrent flow of hot gases.
As it descends, coal is first dried and then carbonized. At the hearth area,
only a residual char composed of carbon and ash remains. The oxygen/steam
mixture is admitted through four tuyures just above the hearth, where the
gasification and combustion reactions occur. Temperatures at the hearth are
sufficiently high to maintain the ash in a liquid state, and the molten ash
drains through a centrally located taphole into a water quench bath. A slag
is produced which resembles coarse sand. It settles to the bottom of a
water-filled lock hopper and is periodically removed.

The flow diagram of the pilot plant system is shown in figure 2. The hot
gases pass up through the fuel bed, heat the coal, and carry the tar, light
oil, water vapors, and the gas produced during carbonization to the gas
offtake. The product gas stream is, therefore, a mixture of desired gas plus
a variety of condensibles and other components. This stream enters a washer
where a spray of the aqueous fraction of gas liquor which is recycled and
cooled condenses water, light oil, tar vapors, and removes entrained dust
particles. Accumulations in the spray washer are periodically discharged.
The gas is then cooled, depressurized, and passed through a coke-filled
scrubber for final cleanup before it is metered. Up to 1 ton/hr of lignite
can be gasified in the unit at a 400 psig operating pressure.

The objectives and capabilities of the GFETC pilot plant program were
expanded beginning in early 1977. Two major changes are involved. The pilot
plant and gasifier are being modified to provide the capability to: 1) oper-
ate continuously for periods of 5 to 7 days, and 2) to test agglomerating
coals. Design of additions or modifications to existing facilities of the
Center was initiated, and construction phases are in progress. The gasifier
will be relocated in an addition to the existing pilot plant in which a
centralized control room and laboratories for effluent-related functions will
be provided, and a conveyor system for unmanned coal charging of the gasifier
is being installed.

Modifications to the gasifier include: installing a stirrer which
operates in the top portion of the bed, and providing a double coal lock
charging system with feeders. A cross-sectional view of the modified gasi-
fier is shown in figure 3. Auxiliary additions include gas liquor sepa-
ration, storage, and incineration, and a nitrogen supply purge system. A
schematic of the modified pilot plant system is shown in figure 4. A con-
ceptual drawing of the gasifier and facility is shown in figure 5.
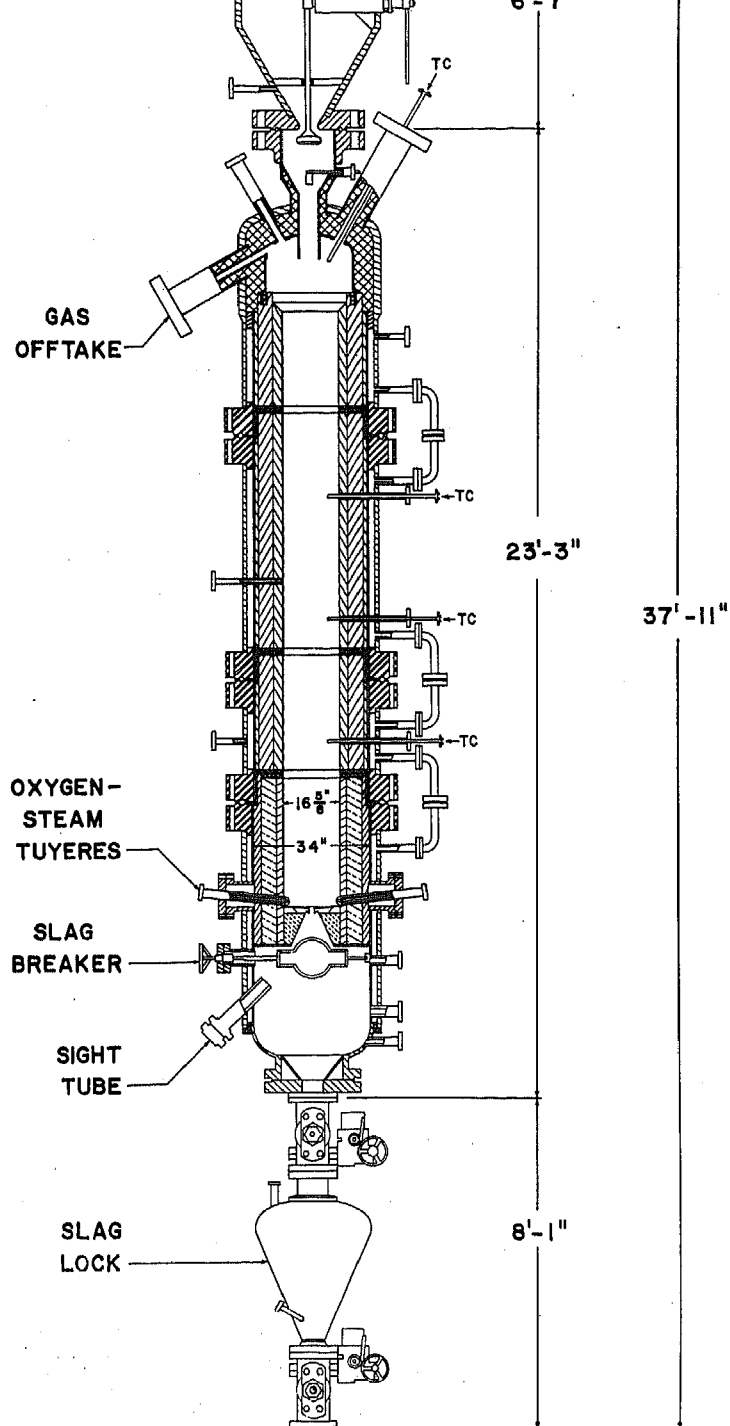
Figure 1. - Cross section of original GFETC slagging gasifier.
Configuration used until September 1978.
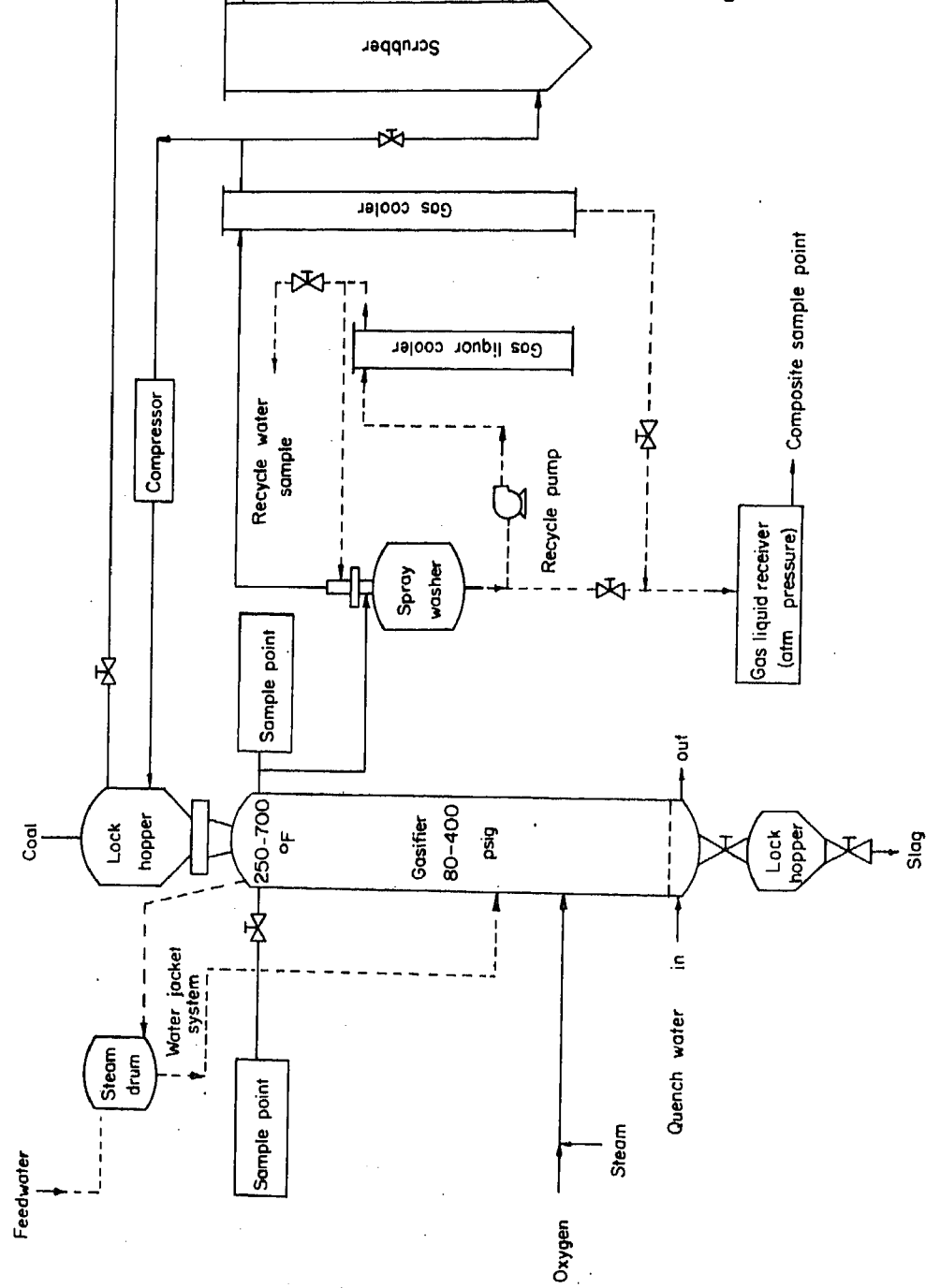
Figure 2. – Process flow diagram for the GFETC slagging gasification pilot
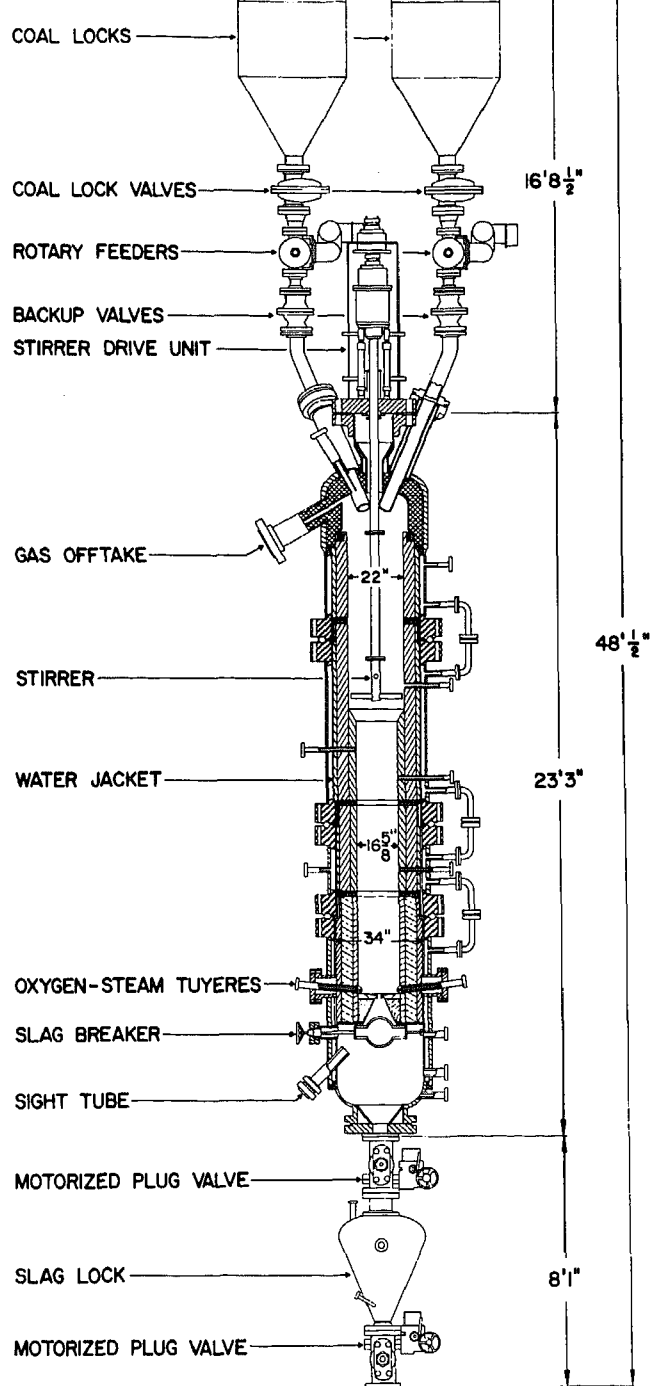
Figure 3. - Cross section of modified GFETC slagging gasifier.
Operation planned for early 1979.

COAL STORAGE

CRUSHING AND
SCREENING

COAL
METERING

NITROGEN SUPPLY

OXYGEN SUPPLY

STEAM SUPPLY

STEAM
DRUM

STIRRER DRIVE

PRECOOLER

GASIFIER

SPRAY
WASHER

TAR

SLAG REMOVAL

EFFLUENT STORAGE

FLARE STACK

GAS METER

SCRUBBER

GAS COOLER

GAS LIQUOR COOLER

TAR-LIQUOR SEPARATOR

GAS LIQUOR

INCINERATOR
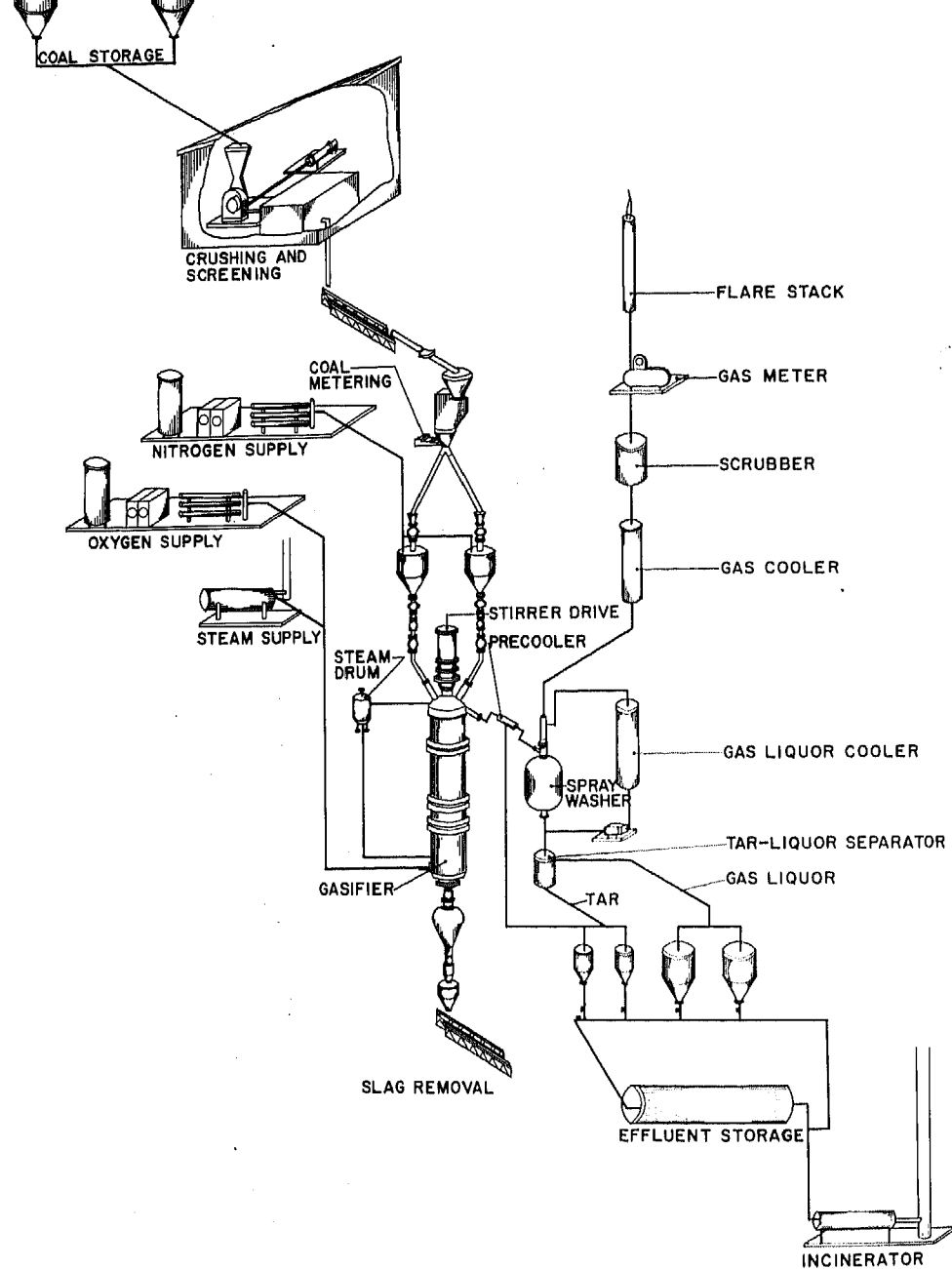
Figure 4. - Schematic of modified GFETC pilot plant.

ANALYTICAL LAB

CONTROL ROOM

LIQUIDS HANDLING
AND STORAGE

WASTE TREATMENT
STUDIES

WORK AREA

Figure 5. - Conceptual view of relocated SFBG and associated facilities.

for operation on bituminous coal, and the temperature of the offtake gas must be reduced prior to entering the spray washer. The precooler will also selectively remove tars and heavier components in the product gas when the lower moisture coals are used.

3. STRATEGIC APPROACH FOR ENVIRONMENTAL ASSESSMENT

The selective approach of the GFETC project is that the primary contribution which data from this oxygen-blown gasifier can make is to the direct application of SFBG technology in SNG plants. The information is expected to be used by future designers and operators, as well as state and federal agencies which are charged with licensing and regulating these plants. Data on specific coals will be made available to the public on gas contaminants, and process-produced tar, oil, and waste water. Since the principal unresolved and controversial problems attending operation of SNG plants are concerned with the treatm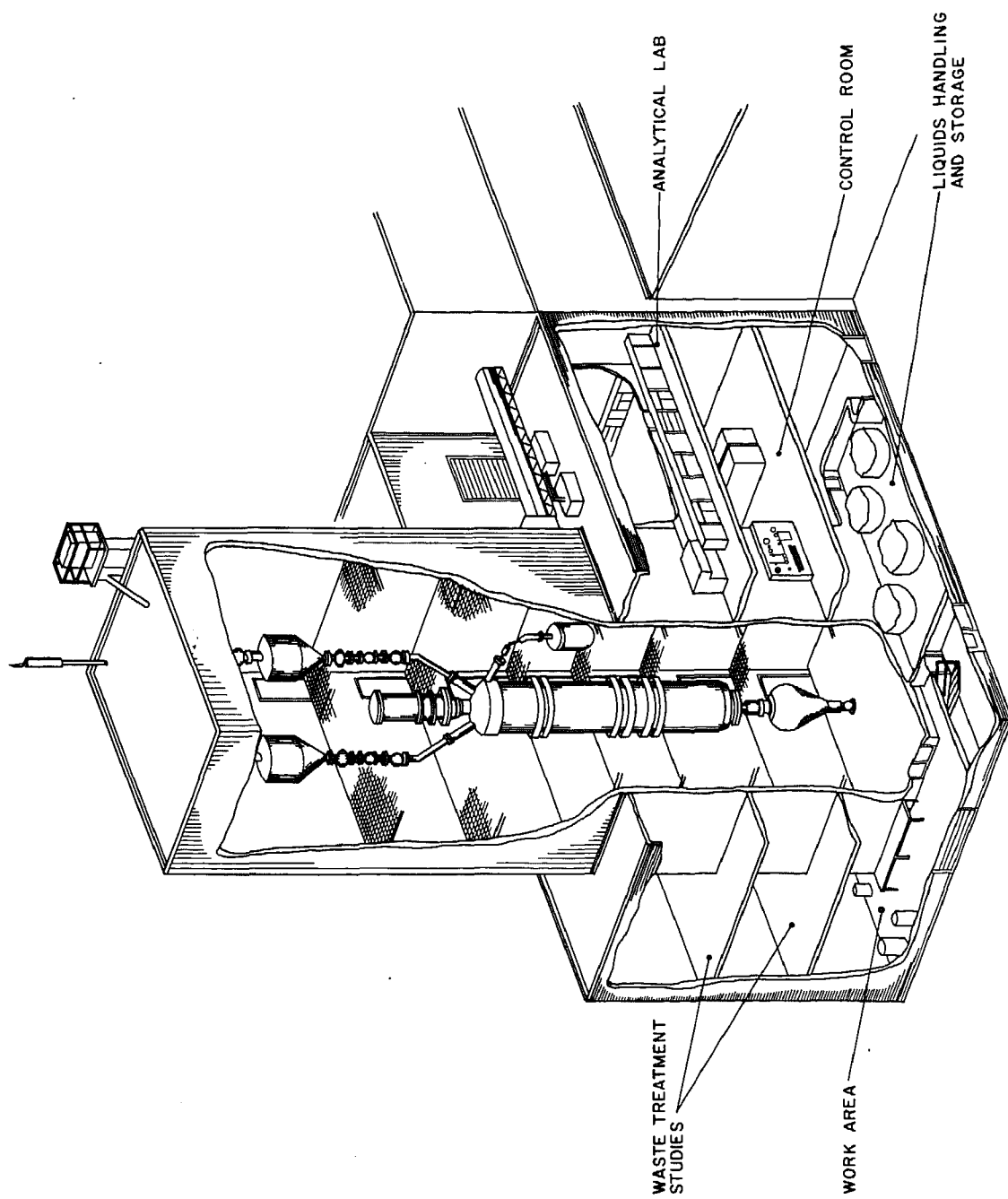ent, use, and disposal of tar, oil, and waste water, studies will be performed to establish treatment techniques consistent with total reuse of water and zero discharge of liquids.

The gas liquors from the SFBG process are produced from the moisture in the raw coal and any process steam not reacted, the tar and oil originating from carbonization of the coal, plus a variety of organics and inorganics which are dissolved in the aqueous condensate. The process streams that result from treatment of gasifier effluents are device-specific -- that is, they depend on the particular hardware that is used. The treatment operations have, therefore, been designed to provide enough flexibility to ensure scaleable data, even in cases where specific hardware used may not be the type selected for future commercial application.

The treatment steps for the aqueous phase currently planned involve: 1) ammonia stripping, 2) phenol extraction, and 3) biological treatment. In addition, it is planned to study the suitability of waste water from various stages of treatment in a simulated cooling tower, the degree of oxidation or evaporation of residual organics, and the fouling of heat transfer surfaces. Studies relating to the tar-oil fraction include characterization and suitability for potential utilization schemes.

The product gas is extensively characterized and analyzed. Studies of gas treatment are underway elsewhere which address points of particular concern (e.g., studies on methanation at the Synthane Plant and at IGT), and the commercial technology is judged satisfactory with minimum refinement. For these reasons gas treatment is not being studied.

Solids produced in a commercial slagging gasification plant would include slag and a variety of sludges produced in water treatments. Slag from the pilot plant will be characterized in respect to analysis and leachability. Sludges, as they are produced in various pilot plant phases of the treatment studies, will be evaluated for potential disposal or utilization.

characteristics and operating conditions will provide guidelines for commercial design.

4.   SAMPLING AND ANALYTICAL METHODS FOR GASEOUS AND LIQUID EFFLUENTS

A major effort has been directed to developing and enlarging the capabilities for characterization of the gaseous and liquid effluents produced. In general, established techniques are verified and progressively modified to the process-specific conditions which exist.

Samples of offtake gas are collected regularly and routinely during operation and analyzed by gas chromatograph with a thermal conductivity detector. The instrument is calibrated with standard gases for: hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen sulfide, ethene, ethane, propene, propane, iso-butane, and normal-butane. Approximately 20 additional hydrocarbons are indicated by GC analysis with a flame ionization detector. These components are being identified, and their determination will become routine. Sulfur gases, hydrogen sulfide, carbonyl sulfide, carbon disulfide, sulfur dioxide, and thiophenes, etc. are analyzed by separate GC with flame photometric detector. Methods are being developed for routine determination analysis of hydrogen cyanide, thiocyanate, and ammonia.

The major effluent stream of interest is the condensible fraction of the product gas -- the water and organics removed from the product gas stream in the gas quenching system. Obtaining representative and reliable scaleable samples has been a principal concern in present studies. Three different sampling methods are used. Method 1 consists of sampling the total quantity of liquids accumulated in the spray washer during each test. Degradation of certain chemical constituents due to system residence time, dilution effects due to the startup water in the spray washer, the effects due to high recycle rate of aqueous fraction, and the inability to collect samples representative of selected time periods are all problems of this method. Method 2 utilizes sampling systems which take a slip stream of the product gas at the gasifier offtake and pass it through a series of cyclones, condensors, and filters to remove the condensibles and particulates from a measured quantity of gas. Continued refinements have been made to solve the problems of sampling a dirty, high-pressure gas stream and to overcome inherent deficiencies associated with Method 1. The specific objective is to provide the capability to collect a reproducible, scaleable representative sample during selected short-time periods of operation.

Method 3 is a different approach to characterizing the production rate of the condensible effluents. It utilizes a gas chromatograph for on-line analyses. The technique being developed performs a simulated distillation of the coal tars produced with the product gas at intervals of 5 minutes. Identification of compounds by groups is being studied and appears to be feasible. This system is demonstrably capable of establishing rapid and short-term variations in tar-oil production rate, and possibly defining composition changes during short-term process upsets.

fractions obtained by vacuum distillation will be individually analyzed. In addition, organic compound identification by high-pressure liquid chromatography, pyrolysis GC/IR, NMR, and UV/Vis spectrophotometry is in progress and will greatly enhance the characterization efforts.

The aqueous phase of gas liquors normally contains ammonia, phenols, and acid gases. Ammonia and phenol are present at concentrations as high as several thousand mg/l. Routinely, the pH, alkalinity, phenol, o and m-p-cresol, ammonia, cyanide, sulfide and total sulfur, total organic carbon, and inorganic carbon content of aqueous phase is determined. Analytical development efforts are currently directed to the determination of trace organics present in the aqueous liquor fractions and as these techniques are established, will be added to the routine analytical base.

Determination of major, minor, and trace elements in effluents in order to establish material and elemental distribution in coal gasification is planned. Data will be reported for selected trace elements, including the following: antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, gallium, germanium, lead, lithium, manganese, mercury, molybdenum, nickel, phosphorous, selenium, strontium, tellurium, tin, uranium, vanadium, zinc, and zirconium. Facilities of the Center include an ICAP analyzer for trace element determinations. At present, verification of procedures for sample preparation and processing are in progress and first efforts on selected samples have been initiated.

5. RESULTS TO DATE ON CHARACTERIZATION OF GASEOUS AND LIQUID EFFLUENTS AND RELATIONSHIP TO OPERATING VARIABLES

Since May 1976, and until September 27 of this year, a total of 66 tests were scheduled with the Grand Forks pilot plant. Feedstock included three lignites and two subbituminous coals ranging in moisture content from 20 to 40 pct. Sustained operation was not achieved in the limited tests on subbituminous coals due to slagging problems or on one lignite of 40 pct moisture content due to the high moisture content. Samples and data in regard to effluent characterization were collected in 30 of the tests, principally on lignite from two mines, Indian Head (Mercer County, Central North Dakota) and Noonan (Burke County, Northwest North Dakota). Pressure was varied from 100 to 400 psi in 100-pound increments, and oxygen flow from 4000 to 6000 scfh, with corresponding steam inputs from 0.9 to 1.1 molar ratio of oxygen to steam.

Progressively, sampling techniques have been modified and refined, and efforts were directed to establishing test reproducibility, operational stability, and variability, particularly during upsets caused by coal charging. Samples from a variety of sampling locations and utilizing different techniques were systematically collected for comparison. Concurrently, analytical methods and techniques have been and continue to be progressively verfied and modified as required.

utilized to produce quantity samples of aqueous liquor for biological treatment studies now underway at two facilities, and extensive effort was made to establish progressive changes in effluent characteristics as a function of operating time. Special effort was also made to determine change which occurred in effluent characteristics during the periodic upsets caused by coal charging and interruption of coal feed. These factors will be much less important in the modified gasifier when test periods of longer duration are possible, and the periodic upset during charging the single lock hopper will no longer occur. However, these data are required in establishing and assessing the validity of data collected in the program to date.

Since termination of operations at the end of September, efforts have been directed to compiling and evaluating the data. Typical fuel analyses for test lignites are given in Table 1. Moisture content of Noonan lignite "as tested" is not representative of the "as received" condition of 36 pct due to moisture loss which occurred in extended open storage, size preparation, and handling over the duration of the test operation. Data given in Table 2 illustrate the composition of gas produced. Both iso-butane and n-butane are now determined and found to be at the 0.01 to 0.02 pct range for gas produced from Indian Head lignite. Operating results at pressures ranging from 100 to 400 psig are given in Table 3. Effluent production of selected components in gas liquor as a function of operating pressure is given in Table 4. Effluent production and characteristics at identical operating conditions are compared for two lignites in Table 5. It is expected that when operations are resumed in the modified gasifier, tests will be conducted on test lots of the same lignites to compare results obtained with double lock feeding to those obtained with single lock operation.

A variety of publications and presentations have been prepared at the GFETC describing general and selected phases of the studies. These are listed as a source of additional information at the end of this paper.

6. PLANS FOR SEPARATION AND TREATMENT OF LIQUID EFFLUENTS

In the past, gas liquor that accumulated in the spray washer was periodically sampled and discharged to an external tank at atmospheric pressure. On completion of a run, all remaining liquor was drained to this tank. Tar, oil, and aqueous phases were decanted and drawn off separately, sampled, and analyzed. The composite end-of-run sample contained the liquor produced during the run and the startup city water required for initial operation.

The composite gas liquors contain an aqueous phase, a floating oil phase, possibly a sinking tar phase, and solid particles of dust, ash, and ungasified coal. Two improvements of the sampling and gas liquor collection system are being planned. The first involves continuous drawoff from the spray washer of two or three different phases--floating oils, heavy (sink) tars, and the principal aqueous phase. Secondly, a precooler will be installed between the gasifier and the spray washer with limited injection of

Proximate, pct:

Moisture........................	37.6	30.3
Volatile matter................	25.7	28.2
Fixed carbon...................	30.5	35.4
Ash............................	6.2	6.1

Ultimate, pct:

Hydrogen.......................	6.9	6.4
Carbon.........................	40.9	45.9
Nitrogen.......................	.5	.7
Oxygen.........................	44.7	40.6
Sulfur.........................	.8	.3
Ash............................	6.2	6.1

Heating value, Btu/lb...........	6780	7670

Ash Fusion Temp., °F:

Initial deformation............	2030	2070
Softening......................	2080	2100
Fluid..........................	2130	2130

TABLE 2. - Typical product-gas analyses

Coal...........................	Noonan	Indian Head
Run Number.....................	RA-31	RA-40

Gas Analysis, pct, N_2 free:

CO.............................	57.3	53.6
H_2..........................	30.5	32.5
CO_2.........................	6.4	8.4
CH_4.........................	5.1	4.9
C_2H_4.......................	.2	.2
C_2H_6.......................	.3	.3
C_3H_6.......................	.09	.06
C_3H_8.......................	.09	.04
H_2S.........................	.1	.2
COS............................	<.01	.01

Heating value, Btu/cu ft.......	340	333

Operating Pressure, lb./sq.in ..	100	125	200	400
Coal............................			Indian Head	
Moisture in Coal, pct...........	22.9	36.4	35.7	38.6
Test Conditions:				
Oxygen rate, std.cu.ft./hr. ..	4,000	4,000	4,000	4,000
Oxygen/steam molar ratio......	1.0	1.0	1.0	1.0
Calculating period, hr.	7.15	6.08	11.92	8.68
Fuel Rate (as-charged), lb./hr..	1,049	1,233	1,259	1,296
Fuel Rate (maf), lb./hr.	729	703	730	728
Product Gas Rate,				
std.cu.ft./hr.	20,108	20,759	21,994	21,039
Slag Rate, lb./hr.	72	55	67	50
Oxygen Consumption:				
cu.ft./1000 cu.ft. gas........	198.9	192.7	181.9	190.1
cu.ft./1000 cu.ft. $CO + H_2$....	224.0	218.7	212.3	230.3
cu.ft./lb. maf fuel..........	5.49	5.69	5.48	5.49
Steam Consumption:				
lb./1000 cu.ft. gas..........	9.45	9.15	8.64	9.03
lb./1000 cu.ft. $CO + H_2$.......	10.64	10.39	10.08	10.94
lb./lb. maf fuel.............	.26	.27	.26	.26
Production, cu.ft./lb. maf fuel:				
Gas...........................	27.58	29.52	30.11	28.89
$CO + H_2$.....................	24.50	26.01	25.80	23.85
Product Gas Composition:				
CO_2...........................	5.0	6.6	8.4	10.5
Illuminants..................	.6	.3	.3	.2
H_2...........................	29.2	31.3	31.5	28.5
CO...........................	59.7	57.0	54.2	54.4
C_2H_6........................	.2	.3	.3	.3
CH_4...........................	4.3	4.5	5.3	6.1

Coal		Indian Head		
Run Number	RA-18	RA-36	RA-33	RA-38
Pressure, lb/sq in	100	125	200	400

lb/ton MAF Coal:

Tar	92	83	73	66
Water	1,044	1,404	1,408	1,378
Ammonia	7.8	9.1	9.6	12.7
TOC	10.0	11.4	12.3	12.9

water to condense tar, but without condensing the aqueous fraction. This precooler will be particularly important in operating on low-moisture (bituminous) coals where the offgas from the top of the gasifier may reach 900° F rather than the 320° F associated with lignite of 30 pct moisture.

The individual phases of the gas liquor must be separated for subsequent treatment. The aqueous phase of gas liquor, with tar and oil essentially removed, contains some suspended matter of colloidal tar/oil, dust, ash, and unburned coal. Ammonia and phenol can be removed by biological action, but past experience has shown that equipment size to provide required time generally precludes biological treatment of these substances at high concentrations. Both ammonia and phenol have market value, and proven commercial processes can successfully recover these from the gas liquor. Studies relating to development of improved techniques for their removal, therefore, have been given a low priority. Sour gas stripping and phenol extraction are being considered, however, as a means of producing representative waste water for biological treatment studies, both before and after phenol and ammonia removal. Although most investigations have been on aerobic digestion, anaerobic biological treatment offers some advantages and will also be considered.

Various physical/chemical processes, such as chemical and polymer coagulation and precipitation, multi-media filtration, activated carbon adsorption, ultra filtration, reverse osmosis, etc., are also candidate treatments to upgrade water qualities from gas liquor. Bench-scale experiments will be performed on selected methods to ascertain their applicability to the SFBG liquors, both as a primary treatment or as a polishing technique.

The major use of treated water at proposed gasification plants is in cooling towers. From an economic standpoint, the less treatment gas liquor requires prior to use in a cooling tower, the better. In any case, removal of tar, oil, and the major portion of the phenol and ammonia would be required prior to use of liquor in a cooling tower. A small pilot-scale cooling tower is being considered to operate on gas liquors as produced in

	RA-31	RA-40
Run Number	RA-31	RA-40
Coal	Noonan	Indian Head
Moisture in Coal, pct.	30.3	34.7
Operating Pressure, lb./sq.in.	200	200

Production, lb./ton maf:

Tar	90	70.2
Water	1,140	1,220
Ammonia	12.6	11.0
Total organic carbon	13.3	12.3

Concentration of Selected Constituents in Aqueous Phase:

pH	9.3	9.5
Alkalinity, ppm $CaCO_3$	30,020	25,410
Ammonia, ppm	10,220	8,440
TOC, ppm	10,000	9,460
Phenol, ppm	5,689	4,260
o-cresol, ppm	1,000	836
m-p cresol, ppm	3,317	1,671

Concentration of Selected Components in Tar Phase, pct:

Phenols	18.2	15.4
Naphthols	3.9	5.6
Dihydroxybenzenes	1.4	0.0
Naphthalenes	9.3	9.0
Aromatic hydrocarbons with 3 to 5 rings	8.5	8.2
Saturated hydrocarbons	10.2	22.0
Non volatiles at 300° C and 0.1 torr	2.4	3.6
Average mol. wt. of volatile compounds	152.2	156.9

7. SOLID AND SLUDGE EFFLUENTS

In a commercial coal gasification plant the slag, or ash produced, is a formidable quantity of material. For example, a 25,000 ton/day lignite facility may produce 2,000 tons/day of slag/ash which must be disposed of. Except for possible use as an aggregate or as a fill for leveling purposes, the probable disposal method for the slag is in a landfill, and most likely it will be returned to the mines from which the coal came. Slag produced in SFBG is believed to be not leachable, but if process water is used for quenching, it may contain leachable components. As leaching to groundwater is not permitted by regulatory authorities, either an extensive sealing operation will be required or the slag, as produced, must be shown to be essentially non-leaching.

The disposal of residual dissolved and suspended inorganic and organic solids from the various waste water processing and treatment streams must also be managed to prevent contamination of surface or groundwater or the atmosphere. It has been suggested that sludges produced may be valuable as soil conditioners and low-grade fertilizers in mine spoil bank revegetation programs.

Blowdown from a cooling tower will be high in dissolved (and possibly suspended) solids which must be disposed of. Some materials in the blowdown may be inherently toxic, as are cadmium and mercury, or they may be merely aesthetically unpleasant, as is iron. Other elements, such as sodium, calcium, and magnesium, may contribute undesirable qualities for use in irrigation, domestic, or industrial water uses. Evaporation of cooling tower blowdown will probably be necessary, either in an evaporation pond or by direct means using waste heat.

The characterization of these solids and wastes will continue at GFETC. Expansion of SFBG studies will utilize, to a large extent, established and on-going programs to characterize the leachability of such wastes and to develop other necessary information.

8. CONTRIBUTION TO ASSESSMENT OF BIOMEDICAL EFFECTS

The gasification of coal produces some materials which have been shown to have toxic and mutagenic effects. Inevitably, small amounts are released to the atmosphere or are brought into contact with workers in a gasification plant. The Grand Forks slagging gasifier pilot plant is a reasonable model for worker exposure, and it provides data that, with proper interpretation, permit environmental emissions to be estimated. The biomedical concerns have generated a large scientific effort. Using a variety of procedures, skin tests, inhalation tests, and gross toxicology, by ingestion and tissue analysis with appropriate test animals, and bacterial mutagenicity, the

to selected laboratories as a contribution to this total long-term effort. In addition, health records will be maintained on workers engaged in coal processing activities at the Grand Forks Energy Technology Center to assist in determining any possible long-term effects relating to occupational exposures.

9. CONCLUSION

The SFBG at GFETC provides the opportunity to assess the environmental effects of fixed-bed coal gasification. Utilizing manageable test lots of coal, representative effluents will be generated for verification of treatment and control processes or development of improved techniques. The capabilities and potential of the modified pilot plant will expand the operational and environmental data base available for commercial development of a viable SNG industry in the U.S.

10. GFETC PUBLICATIONS ON THE SFBG

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5. Schobert, et al. "Petrochemistry of Coal Ash Slags. 1. Formation of Melilite and a High-Temperature Glass from a Calcium-Rich, Silica-Deficient Slag." Joint CIC-ACS Conference, Montreal, 1977.

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7. Ellman, et al. "Current Status of Studies in Slagging Fixed-Bed Gasification at the Grand Forks Energy Research Center." Ninth Biennial Lignite Symposium, Grand Forks, 1977.

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OVERVIEW OF THE SYNTHANE PILOT PLANT ENVIRONMENTAL ASSURANCE PROGRAM

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ABSTRACT

An historical account of the development and current studies of environmental monitoring and compliance at the SYNTHANE pilot plant will be presented. This account will include the experiences and problems in establishing monitoring programs in the following areas:

Air:
    Ambient Monitoring
    Stack Testing
    Fugitive Emissions

Noise:
    Background
    In Plant

Water:
    Surface Water Control
    NPDES* Sampling
    Continuous Water Monitoring
Occupation Health:
    Problem and Direction

Solid Waste:
    Characterization
    Disposal

In February and March 1975 the first ambient air background studies were undertaken at the SYNTHANE pilot plant. Subsequent to these initial studies an environmental monitoring and compliance program was developed incorporating the areas noted above. The cost of this program to date plus facilities and equipment amount to approximately three (3) million dollars. The experience provided in interfacing with the technology development and developing the environmental monitoring and compliance program can be of value to all who are involved in small scale and large scale development.

*National Pollutant Discharge and Elimination System.

The Environment & Conservation Division of the Pittsburgh Energy Technology Center, Department of Energy, was formed on July 1, 1975. The charter under which this division operates in the environmental area focuses on the assessment of pollution potential from coal conversion processes and the evaluation of alternative techniques for reducing the environmental impacts of these technologies. This paper presents an overview of the comprehensive monitoring and assessment of the SYNTHANE pilot plant.

As of December 1, 1978, US DOE Headquarters terminated operations at the SYNTHANE pilot plant. Subsequently the majority of the programs discussed in this report have been or will shortly be discontinued. This report will attempt to highlight important considerations in designing and implementing an environmental monitoring program for other pilot plant operations.

The major assessment efforts can be appropriately divided into five areas in which most environmental legislation is also categorized--air, water, noise, solid waste and occupational health.

Process Description

The 72 T/D SYNTHANE Coal Gasification pilot plant converts coal to high BTU synthetic pipeline gas. Basically there are five major steps in the process: (1) pretreatment, (2) gasification, (3) shift conversion, (4) purification, and (5) methanation.

Pretreatment: The coal is crushed to -20 mesh, dried with hot flue gas generated from the combustion of No. 2 fuel oil, then pressurized in lock hoppers with CO_2. It is then pretreated at operating pressure with a steam-oxygen mixture. This mild oxidation destroys the caking properties of the eastern coals so that they do not agglomerate in the gasifier.

Gasification: In the free fall coal feed mode of operation the coal overflows the pretreater into the gasifier, about 20 feet above the normal bed level. The coal falls through the hot gases rising from the fluidized bed and is partially devolatilized. When utilizing the deep bed injection mode the coal is fed below the top of the fluidized bed. In either mode steam and oxygen enter the gasifier just below the fluidizing gas distributor. The gasification reaction occurs in the fluidized bed. Char containing ash and unreacted carbon is transferred to a separate bed in the lower part of the gasifier vessel where it is cooled before being discharged to lock hoppers.

The product gas, containing methane, hydrogen, carbon monoxide, carbon
dioxide, and impurities, is passed through a venturi scrubber and a scrubber
tower to remove carry-over ash, char, and tars.

*Shift Conversion and Purification: The concentration of hydrogen and carbon
monoxide in the gas is then adjusted to a three-to-one ratio in the shift con-
verter by the reaction of CO with steam to produce H_2+CO_2. The acid gases are
absorbed in a hot-potassium-carbonate tower (Benfield process); carbon dioxide
is reduced to below 2% and sulfur is reduced to 40 parts per million. (Re-
generation of the potassium-carbonate solution produces a gas rich in hydrogen
sulfide which is converted to elemental sulfur by the Stretford process). The
remaining traces of sulfur in the product gas are removed by passing the gas
through activated charcoal.

*Methanation: Two systems for methanation of product gas were planned for
testing--hot gas recycle (HGR) and tube wall reactor (TWR).

I. Ambient Air Monitoring

   A. Background Study

   The ambient air monitoring program for the SYNTHANE pilot plant began with
an initial background study of the air basin in which the plant was sited.
This initial phase was performed in February and March 1976 and served to pro-
vide a background data base with which to compare ongoing monitoring data as
the pilot plant began operation. The background study consisted of the
following data collection activities. The results of these data comparisons
are available through the EC Division.

   Four Hi Vol samplers were operated for a 24- hour period every six days.
The locations are shown in Figure 1. The Hi Vol filters were weighed and
analyzed for the following constituents: fine particulates, sulfates, nitrates,
mercury, arsenic, nickel, lead, beryllium and cadmium. The prevailing 24-hour
surface wind from Allegheny County Airport, located approximately 3.5 miles
from the air monitoring network, was computed for each test along with other
meteorological dispersion parameters. The data were then compared with all
federal and state ambient air standards and analyzed to determine what the
plant contribution was to the monitors.

*The Shift Conversion and Methanation process steps were not operated
 throughout the life of the SYNTHANE pilot plant.

An eight-station sulfation plate network was operated utilizing fifteen-day exposure periods. The sulfation data was converted to PPM SO_2 by dividing the average sulfation rate of three plates located near the continuous SO_2 monitor at Site 1 into the average hourly SO_2 concentration for the fifteen-day period. This number was then converted to ug/m^3 SO_2 by multiplying it by 2620. The data were compared with annual ambient SO_2 standards and then analyzed to determine the plant contribution.

A dustfall network was utilized consisting of eight site locations. The dustfall jars were collected once a month and analyzed for total dustfall, water soluble particles and water particles. The results were compared with Pennsylvania State ambient standards.

In addition to the stationary sites a mobile van sampled the air basin. See Appendix A.

B. Six Month Air Quality Study

The second phase of the air monitoring program conducted August 1976 to January 1977 consisted of a six month study to assess the pollutant contribution of the pilot plant operation to the ambient air. These monitoring data were compared to the background data base to evaluate any change in the air basin. The method of data collection and parameter measurement for the six-month study was essentially the same as for the background study.

The pilot plant contributions to the Hi-Vol samplers were determined by plotting the prevailing 24-hour wind for each Hi-Vol unit on a map showing the location of each monitor and the SYNTHANE plant. A triangular area is drawn along the radial of the prevailing wind from the plant. The width of the triangle is a 15° arc on either side of the prevailing wind radial. (Note Figure 1.)

Monitoring parameters included CO, O_3, NO_x, SO_2, Total Hydrocarbons (THC), H_2S, Coefficient of Haze (COH), wind speed and direction, dew point and temperature. Under worst case assumptions, the concentrations at any monitoring site within this triangle measure the plant emissions. All other monitoring sites are considered to measure background. The difference between the average downwind concentrations and the average upwind concentration is considered to be the plant contribution. This of course is a worst case assumption which assumes that no other source exists between the plant and the receptor site. Extra care should be taken in interpreting the data with this assumption in mind.

AIR
QUALITY
SAMPLING
NETWORK

HI-VOL DATA

FINE
PARTICULATES
SULFATES ④ SITE NO
NITRATES

RUN NO: 25
DATE: 12/24/76

GROUND INVERSION
STRENGTH 2.4 °C
TOP 1600 FT. MSL
DURATION

UPPER LEVEL INVERSION
STRENGTH °C
BASE FT. MSL
TOP FT. MSL

AFTERNOON VENTILATION
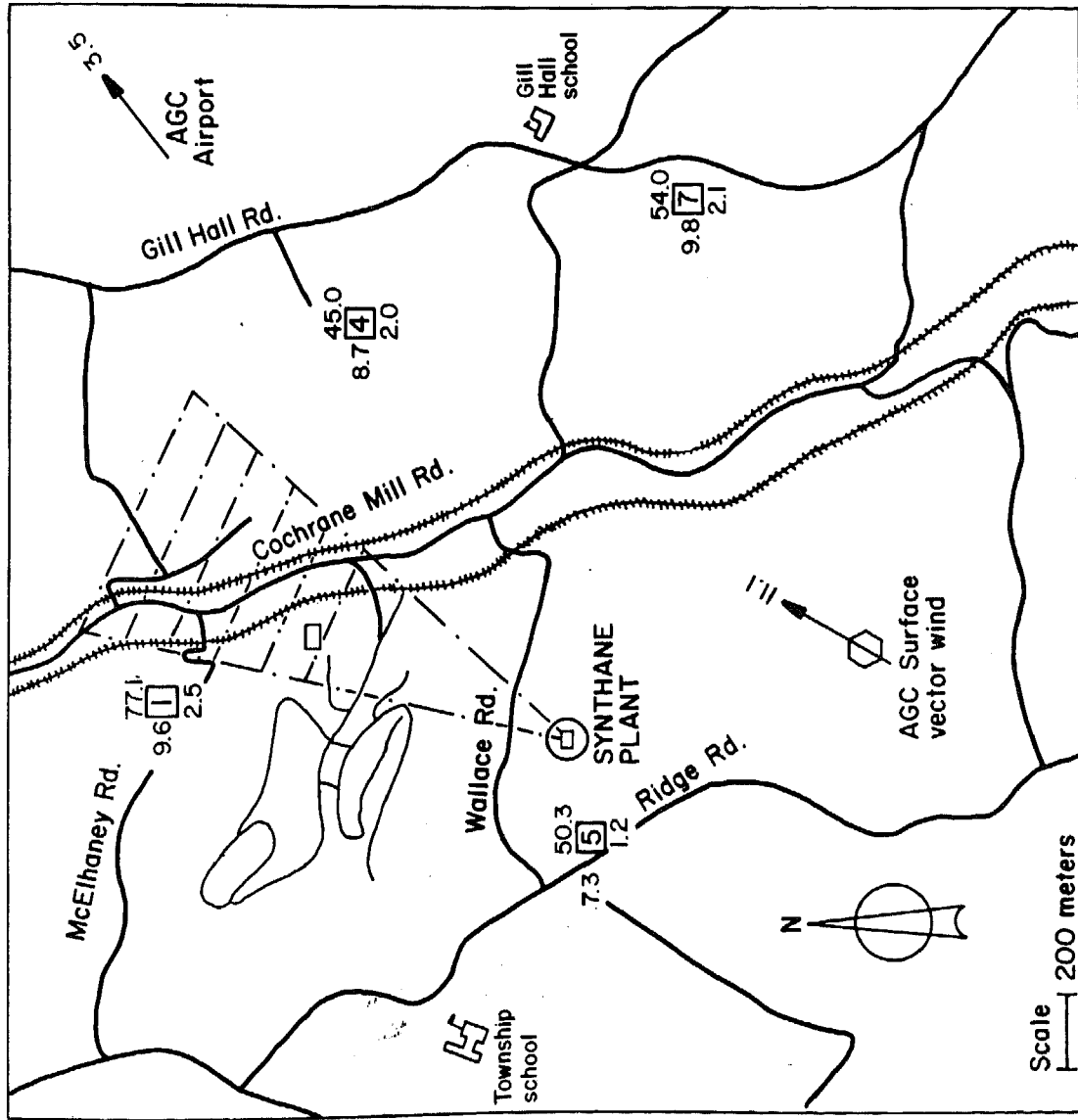RATE 6400 M3/g

2-7-79 L-16496A

Figure I - Ambient air monitoring sites

C. Continuous Monitoring Trailers

The background and six-month study provided a data base to evaluate the pilot plant contribution to the ambient air under certain operating conditions. However, the nature of pilot plant operations are such that changing conditions were anticipated to change emission characteristics. Some parameters affecting effluent characteristics include types of coal (high and low sulfur content), temperatures, pressures and fuel feed characteristics.

To properly evaluate these changing conditions, a continuous monitoring network was determined to be most cost effective as well as efficient. Two ambient air monitoring trailers were subsequently sited and put into operation in early 1977. Records containing SYNTHANE pilot plant operations data were maintained to compare with the data generated from the monitoring trailers. The correlation of these two information sources provided a means of evaluating changing process conditions relative to the ambient air.

The Hi-Vol samplers, dustfall jars and sulfation plates were retained from the background and six-month study as part of the continuous monitoring net-work. The only change in these data collection systems was analysis of the metals on the Hi-Vol filters. These were changed to provide a full survey for all metals potentially emitted from the pilot plant and to correlate them with the source testing.

The site source of the trailers were determined using the meteorological data base of the background and six-month study. The prevailing wind was delineated and one trailer was located upwind and one downwind of the plant. Physical interferences such as buildings, trees and hills were taken into con-sideration, as well as accessibility.

D. Stack Testing Program

Coordinated with the ambient air monitoring program was a source testing program. The primary emission source on the SYNTHANE pilot plant site was the thermal oxidizer. At the initiation of the program, April 1977, all of process wastewater and gases generated by the plant were combusted in the thermal oidizer. The source sampling served to measure the concentration of various pollutants emitted from this point source. Attempts were then made to compare this information with ambient pollutant concentrations as determined by the air monitoring network. The source sampling program also served to demonstrate compliance to source emission standards. The parameters measured were as follows:

Elemental Analysis	Carbonyls

Elemental Analysis

Arsenic
Beryllium
Cadmium
Fluorine
Iron
Lead
Nickel
Selenium
Titanium

Carbonyls

Nickel carbonyl
Iron carbonyl

Other Effluent Contaminants

SO_2
NO_x
H_2S
Organics
Particulates

Sampling and analytical procedures are noted in Appendix B.

Fugitive Emissions

The Fugitive Emissions Program was planned at the SYNTHANE pilot plant. An inventory had been performed in March, 1978 but no sampling had been undertaken due to the pilot plant operating schedule. Sources that were considered included: baghouse, char pond surface, oil water sump, decanter safety flare, high pressure valves, coal grinding vent system, slurry/filter feed tank, CO_2 vent, wastewater receiver tank vent and open top holding tanks. The actual sampling was expected to begin during the early months of 1979.

II. Water Monitoring

The water monitoring program conducted at the SYNTHANE pilot plant consists of three phases--Surface Water Control, NPDES Sampling and Continuous Water Monitoring.

Surface Water Control

The surface water control program was designed to minimize contamination of site effluent from spills and non-point source discharges. It has become an integral part of the Spill Control and Countermeasure Plan (SPCC), as well as the water pollution control program. Pilot plant operations are characterized by frequent maintenance procedures. This results in unusually high potential for spills to occur and debris to accumulate in process areas. These characterics added to the inherent coal handling problems present a potentially significant surface water contamination problem. In an attempt to mitigate

pollutant loading in the plant effluent, paving and trenching of the process area was undertaken. The concrete paving was sloped to a trench and covered with an iron grill. The trenching carries the surface runoff to two holding tanks (15,000 gal each). The original plan was to collect the surface runoff in the tanks and upon accumulation to analyze the water. If the analysis fell within a specified range the water could be discharged as a batch process. The original plan also provided that during extended periods of rain the initial runoff could be collected in the holding tanks. After the runoff has been washed clean, a valve would redirect the water runoff directly to the storm sewer. As experienced at the pilot plant the effective execution of a surface water control program requires good housekeeping, strict control procedures and close surveillance to minimize the amount of contaminated runoff.

NPDES Sampling

The Code of Federal Regulations, Title 40, requires that owners or operators of a facility discharging via a point source must possess a National Pollutant Discharge and Elimination System (NPDES) permit. This NPDES permit includes effluent limitations to which the owner or operator must demonstrate compliance through a routine sampling and analysis program.

The SYNTHANE pilot plant was issued a NPDES permit, effective July 28, 1977, by the U.S. EPA. Recently the NPDES program has been reorganized whereby the administrative responsibilities are being assumed by the Commonwealth of Pennsylvania, Department of Environmental Resources. This change in adminis-trative responsibility from federal to state levels has already evolved in most other states. The reorganization is expected to change some permit parameters. The permit currently contains discharge limitations for five effluent points. These include a sewage treatment plant, cooling tower blowdown, demineralizer, boiler blowdown (high and low pressure). These five discharge points have been determined to include all discharge contributions to the receiving stream. The justification for this decision was delineated in a December 4, 1975 memorandum to U.S. EPA. The EPA regional office agreed that the PETC proposed sampling sites were more feasible and representative than the single sampling point originally proposed by EPA.

Continuous Water Monitoring

The initial siting of the SYNTHANE pilot plant included the excavation of the valley in which the plant is situated which resulted in the diversion of the natural drainage through a 48" interceptor line, Figure 2. The pilot plant was then constructed over this interceptor along with a 15" storm drain and a 12" perforated drain. The five pilot plant discharge points (previously outlined in NPDES Section) contribute to these three underground drains and are subsequently mixed to form a single effluent stream in a 10' x 10' x 10' concrete box that is located (underground) at the eastern boundary of the pilot plant.
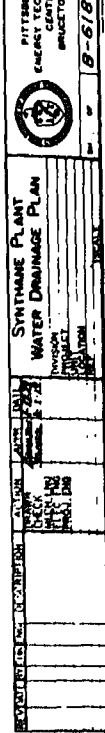
The approach taken to characterize the pilot plant contributions to the receiving stream includes five continuous water monitors, one at the plant inflow at the 48" line, one at the discharge end, one each at the 12" and 15" lines and one to measure the combined flow of the 10' x 10' x 10' concrete box. Flow measurements have been attempted at both inflow and outflow. At this time the "other sources" (storm drainage and road runoff problems) that have contributed to the total plant runoff are being separated out by a rerouting of surface water drainage lines. This source contribution has complicated sampling by blocking lines and interfering with flow measurements. Upon completion of this rerouting of storm drainage and road runoff the original continuous sampling schedule was to be resumed.

At the present time the continuous monitoring network consists of one 24-hour continuous sampler and flow meter at the plant inflow and three continuous samplers plus a flowmeter at the outfall. The samples are visually inspected and general pollutant analyses are performed if determined necessary. The analysis could be performed by the on site Lummus Lab or through a local university contract.

Parameters measured in the water monitoring program for most sampling points include: biological oxygen demand (BOD-5), fecal coliform, conductivity, oil and grease, phenol, pH, NH_3, suspended solids, total dissolved solids (TDS), chemical oxygen demand (COD) and iron.

III. Noise

The noise monitoring program at the SYNTHANE pilot plant consisted of two phases: an ambient noise assessment and an inplant noise assessment.

Synthane Plant — Water Drainage Plan

Surface water from Wallace Rd.

Sanitary treatment plant

Perforated 12" drain

Char pump area

Fuel oil tank

Surface water

Meter pit

Coal pit

Trenchs

Open drainage ditch

Surface water from Wallace Rd.

Perforated drain starts here

Acid mine water

Horse farm

Cooling tower

O2 plant

L.P. CO2

RD

SS

15" SS

10" SS

12"

48"

54"

24"

21"

12"

Scale, feet
0   40   80

LEGEND

—— Oily water sewer
—— Drains to 48" diversion pipe
—— Drains to 15" storm sewer
---- Perforated drain & direct drains
—— Not perforated drain lines

A – Administration building
B – Maintenance building
C – Neutralizer pit
D – Utility building
E – Control building
F – Compressor building
G – Analyzer house

B-618

Ambient Noise Assessment

A background noise assessment was conducted for the SYNTHANE pilot plant during September-October 1977. The concern in this program phase was strictly in regard to the noise emission from the plant rather than with respect to any of its operating characteristics. The principal noise producers in the plant were divided into the following categories:

Mechanical: grinders, pulverizers, gears, conveyors.

Flow Devices: fans, blowers, compressors, valves.

Combustion: furnaces, flares, heaters.

Electromechanical: generators, motors, transformers, circuit breakers.

Augmenting the operating noises were noises produced by maintenance operations and those resulting from truck movement.

A two-step approach was utilized in acquiring the needed data. The first step was field recording of the noise and the second was laboratory analysis of the recorded data.

The field recording system consisted of a sound level meter, a battery powered tape recorder, and an acoustic signal generator for providing the necessary reference signal. A windscreen was used over the input microphone to eliminate wind generated noise. Recordings were not made whenever the wind speed exceeded 15 miles per hour. The frequency response of the sound level meter was set in the A-weighting mode, as this practice will tend to reduce chances of either overloading the sound level meter or saturating the magnetic tape. The sound level meter also served as a calibrated attenuator for the tape recorder. On playback, the signal from the tape recording was fed through a calibrated attenuator into a level recorder. The signal coming out of the level recorder was then sorted by a distribution analyzer into various level intervals. A 5 dB interval was chosen for this study.

The tape recorder had a dynamic range of about 45 decibels. By appropriately adjusting the input level at the start of a recording session, overloading was never observed. The period of measurement spanned the better parts of September and October. The data were tabulated to enable any future correlation of the noise data with the plant operation log and other pertinent environmental data.

The data revealed that noise emission from the plant has a significant impact upon an area as far as about a mile to the east of the plant. It was also determined that a flare stack located atop the thermal oxidizer was a significant contributor of noise emissions. The flare subsequently was modified to reduce the venturi effect and the noise level was reduced to an acceptable level. This noise monitoring program has made it apparent that much lower noise levels are required in rural areas where ambient levels are generally low. The variability of noise level tolerances due to background levels should be an important consideration in siting plant operations.

In-Plant Noise Assessment

The in-plant phase of the noise monitoring program was planned and awaited resumption of the pilot plant operations. The initial monitoring and data collection was expected to begin in Fiscal Year 79. Equipment which was to be used in this study included: precision sound level meter with octave band analyzer; tape recorder, real time noise analyzer; and strip chart recorder. The in-plant noise assessment was to concentrate on the areas categorized in the ambient noise assessment section of this paper.

Occupational Health Program

Many of the occupational health programs for coal conversion processes have been based on the literature documenting hazards of coke oven emissions. Coke oven emissions and coal conversion emissions are considered by some experts to be similar in various categories. It is generally viewed by these health scientists that it would be prudent to develop model occupational health programs similar to those used in coke oven hygiene programs until a knowledge of the specific hazards can be discerned. The investigations to determine the specific worker health hazards of the SYNTHANE process have been underway. Included in these investigations were industrial hygiene type monitoring and biological laboratory testings. Until specific hazards and problem areas were known, protective clothing was worn by workmen who were exposed to potentially hazardous waste products and emissions.

operations were also considered for use or proposed in the SYNTHANE program.

The SYNTHANE pilot plant program was assessed in preparation of "Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants", prepared by Enviro-Control for NIOSH.

Solid Waste Program

The recent passage of the Toxic Substance Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA) has made it increasingly evident that more attention must be made to acceptable disposal and handling of solid wastes. The solid wastes program at the SYNTHANE pilot plant has accelerated in recent months. This acceleration included a project conducted by the EC Division, evaluates solid waste products for toxicity, leachability, mutagenicity and carcinogenicity. This is being conducted through carefully controlled laboratory studies. Leachate studies have been completed on specific waste products in the past. These studies indicated that char pond solids have the potential to create a leachate problem and require special handling. Studies have been conducted on the dewatered char from the SYNTHANE process. This char has been determined to cause no leachate problem and may be disposed of in conventional landfill operations. Data from biological testing concerning the mutagenicity of coal tar products from the SYNTHANE pilot plant process are expected shortly. These data will define parameters for more advanced toxicity testing to provide for environmentally sound disposal practices.

SUMMARY

The U.S. Department of Energy (DOE), as part of our country's overall efforts to address and resolve energy issues, has engaged in a broad range of R&D activities. A major emphasis of these efforts has been focused on the utilization of coal as an energy source. Coal conversion technology is currently developing in several specific areas. The objective of this paper has been to discuss the environmental activities related to one specific coal conversion process referred to as the SYNTHANE Coal Gasification Process.

plant can serve as guidelines in developing similar programs at other pilot or demonstration units. Consideration of problem areas identified at SYNTHANE will be useful as a preventive tool to be utilized in the design and implementation of these similar programs

Some highlighted considerations in conducting environmental assurance programs as identified through the SYNTHANE environmental efforts appear in Appendix C.

DOE has assumed the major responsibility for environmental health aspects of its technologies. This includes the evaluation and assessment of the environmental impact of each developing technology, such as SYNTHANE. The overall practicability and commercialization of these energy technologies depend heavily on their ability to comply with existing and future environmental/health regulations. It seems prudent to assess and develop simultaneously the environmental control technologies and process technology. The early incorporation of environmental concerns will serve to minimize the ultimate environmental impact and perhaps reduce or eliminate the expense of retrofitting control devices on the final process.

Sampling methods utilized in the mobile van data collection activity:

1. SO_2 – one hour impinger samples at 840 cc/min. using West-Gaake
    Absorbing Reagent. Analysis was by colorimetry using pararose-
    aniline-formalhyde-Method B.

    REF. Method 42401-01-69T – Intersociety Committee Methods of
          Air Sampling and Analysis.

2. H_2S – one hour impinger samples at 1.30 1/min. using cadmium hydroxide
    slurry as absorbing reagent. Analysis was by colorimetry of methylene
    blue produced by the reaction of sulfide with reagents.

    REF. Method 42402-01-70T – Intersociety Committee Methods of Air
          Sampling and Analysis.

3. Phenol – one hour impinger samples at 1.85 1/min. using 5% sodium
    carbonate as absorbing reagent. Analysis was by colorimetry using
    4-aminoantipyrine reagent.

    REF. Standard Methods for Water and Waste Water Analysis, 13th.
          Edition.

4. Coefficient of Haze – Particulate was sampled using the AISI Paper
    tape sampler.

    REF. ASTM D-1704-61 – Standard Method of Test for Particulate Matter
          in the Atmosphere.

1. Due to the high temperatures present in the thermal oxidizer stack, a water-cooled sampling probe was used. The portion of the probe not exposed to the high temperatures was heated to prevent condensation.

2. Due to difficulties encountered rigging the traditional probe/impinger box configuration, a heated teflon house was included to allow a flexible connection between the sampling probe and impinger box. The hose temperature was maintained at 250°F or greater to prevent condensation. Acetone washing from the hose was included with that of the probe.

3. Sampling for fluoride emissions (Method 13A) was combined with the particulate sample. A stainless steel screen filter support was used rather than a fitted glass type. The glass support has been shown to retain fluoride (Amendments to Reference Methods 13A and 13B, Federal Register, Vol. 41, No. 230, Nov. 29, 1976, Title 40, Part 60). Test methods and procedures for 13A and 13B appear in the Federal Register, Vol. 40, No. 152, Aug. 6, 1975.

4. The third impinger contained caustic, rather than being dry, to collect arsenic and to protect equipment from acid gases.

Metals

Arsenic, beryllium, cadmium, lead, and nickel contents of the particulate catch were determined by atomic absorption. Impingers 1, 2 were also ether-chloroform extracted to determine condensible organics.

NO_x

U.S. EPA Method 7 was utilized. The sampling train equaled that of Figure 7-1 of the Method.

SO_2, H_2S

SO_2 by U.S. EPA Method 6 and H_2S measurements were combined, according to the State of Texas procedure. The sampling train equaled that of the procedure except the glass fiber filter had to be omitted due to the high temperature. However, the catch was filtered using a glass fiber filter prior to analysis. A quartz sampling probe was substituted for the pyrex due to high temperatures.

Since the State of Pennsylvania requires a different SO_2 analysis, the sampling and analytical procedures followed the APCD, County of Los Angeles, Method for Oxides of Sulfur, page 85, Source Testing Manual, 1965. The in-stack thimble had to be omitted due to the high temperature, but the catch was filtered using a glass fiber filter prior to analysis.

as identified through the SYNTHANE environmental efforts:

Proper segregation of contaminated wastewater from other aqueous effluents. This will facilitate optimum sampling accessibility and representativeness and minimize the volume of wastewater requiring treatment.

Precise documentation of operations schedules concerning air emissions. This documentation is necessary to correlate field ambient air monitoring with operations emissions to yield meaningful evaluations of various pollutant impacts from specific point sources.

Appropriate considerations of community noise levels in conducting the site selection process. Siting in the vicinity of a residence with conservative background noise levels has a much greater adverse impact than an area with higher community noise levels.

The types of solid waste generated by the plant should be considered in the siting process. Certain types of waste require special disposal techniques and facilities. The proximity of the appropriate disposal facilities is important due to high transportation costs and stringent DOT and EPA regulations.

Chairman: Stephen Freedman

Co-Chairman: Jerry Pell

by

J. S. Halow, U. Grimm, J. S. Mei

U.S. Department of Energy
Morgantown Energy Technology Center

A program was initiated late last year at the Morgantown Energy Tech-
nology Center, Department of Energy to demonstrate a 90 percent sulfur reten-
tion capability in the 18-inch atmospheric fluidized-bed combustion (AFBC).
This program was undertaken in response to concerns about the impact of possi-
ble New Source Performance Standards (NSPS) proposed by the Environmental
Protection Agency in sulfur emissions. A high volatile bituminous coal with
4.42 percent of sulfur content was selected for this study. Greer limestone
as well as tymochtee dolomite were used as bed material and sorbent. Combus-
tion tests were carried out at various operating conditions to develop AFBC
engineering and emissions data on this high sulfur coal. Ninety or greater
percent of sulfur retention was attainable in several of the eighteen balance
periods depending on operating conditions. The results of the present tests
clearly demonstrate that the proposed new standards for sulfur dioxide emis-
sions can be met by AFBC's. The required operating conditions could, however,
have serious impact on AFBC economics.

GAS TURBINE CATALYTIC COMBUSTORS FOR COAL DERIVED FUELS

Warren W. Bunker
U. S. Department of Energy
Energy Technology

Catalytic combustion for gas turbines is a unique process which promises
very low NO_x emission levels at high efficiencies and comparable pressure drops.
The Department of Energy (DOE) is expanding the catalytic work of EPA and NASA
into the area of coal-derived fuels, both gases and liquids. On-going programs
for the combustion of low Btu gas, medium Btu gas, and heavy liquids are de-
scribed. Future plans for possible field tests are discussed.

Gerald Goblirsch and Harvey Ness

U.S. Department of Energy

Grand Forks Energy Technology Center

The atmospheric fluidized-bed combustion of Western and Gulf Coast lignites and subbituminous coals offers a method of utilizing these low-sulfur, high-alkali coals with possibly little or no added sulfur sorbent. Tests using a 60inch atmospheric fluidized-bed combustor showed that eight of ten Western coals could be burned without addition of limestone and meet the standard of 1.2 lb SO_2/MM Btu. The downward revision in the NSPS will change the design criteria for these low-rank coals, as well as high-sulfur bituminous coals, but the sulfur retention on ash will still make a substantial contribution.

For the low-rank coals tested, the calcium-to-sulfur ratio ranged from 1 to over 4, and the sulfur retention from nearly 0 to over 90 pct. Reinjection of primary cyclone fly ash increased sulfur capture significantly, but not sufficiently to insure compliance of all low-rank coals under the NSPS standards. Bed temperature influenced sulfur retention in the range of 1250° to 1600°F, with maximum retention at 1400°F without ash reinjection and 1500°F with ash reinjection. During operation some of the coal ash agglomerated within the bed and was also deposited on the tube walls.

Tests for characterizing gaseous and particulate emissions from the AFBC have been performed; preliminary results of these tests are presented in this paper. The physical and chemical characteristics of the fly ash produced in the AFBC with and without cyclone ash recycle are examined.

CONTROL OF NITROGEN OXIDE EMISSIONS IN COAL-FIRED, OPEN-CYCLE MHD POWER PLANTS

Joseph Epstein

U. S. Department of Energy

Energy Technology

The control of nitrogen oxide (NOx) emissions from coal-fired power-plants, including Magnetohydrodynamic (MHD) systems is an issue which most often appears in the evaluation of a new technology. Since the 1960's, the MHD community has given considerable attention

Present information indicates that both current and future NOx standards can be met by the MHD process even though no credit is provided for the significant increase in net plant efficiency over conventional power-plant systems.

Presently available results from experiments as high as 8 MWt and from calculations based on experimentally derived kinetics data have served to empirically identify realistic NOx control techniques. The preferred system operation is to: (a) operate the coal combustor fuel rich, (b) cool the gas slowly in a radiant boiler downstream of the MHD channel/diffuser, (the radiant boiler is the key component in MHD NOx control), and (c) add additional air to the radiant-boiler exhaust, at a temperature high enough to complete combustion but,low enough to minimize the tendency to form additional NOx. These concepts are discussed in detail along with experimental and analytical results that have been obtained to verify that the method of control is technically sound and practical. Current DOE-sponsored R&D efforts are aimed at optimizing the method and at formal demonstration in suitable facilities.

CONTROL OF SULFUR DIOXIDE AND PARTICULATE EMISSION IN MHD POWER SYSTEMS USING HIGH SULFUR COAL

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Argonne National Laboratory

Joram Hopenfeld
U.S. Department of Energy
Energy Technology

W. Spurgeon

Gilbert Associates

MHD power generation systems offer an attractive opportunity to utilize high sulfur coal and yet reduce the emissions of sulfur oxides as well as the oxides of nitrogen and particulate matter. Interaction of sulfur compounds with the potassium seed material added to the coal or combustion products to make the MHD process work results in an attendant reduction of SO_2 emissions of 80 to 90 percent. The sulfur compounds released in the combustion of coal interact with potassium forming solid potassium sulfate. The potassium must be recovered in an MHD system and reprocessed in order to

the interaction of potassium compounds with coal slag, are presented. These results are compared with available experimental information, which summarizes the effectiveness in which SO_2 emissions are compared to present EPA standards, as well as anticipated emission standards for SO_2 in the future. Finally, some comments are made as to the applicability of this control measure as a retrofit means to control SO_2 emissions in existing utility boilers.

FLUE GAS CLEANING FOR PRESSURIZED
FLUIDIZED-BED COMBUSTORS

Irvins Johnson et al.

Argonne National Laboratory

Studies underway at ANL to clean up the hot flue gas from a PFBC so that it will be suitable for gas turbine use will be reviewed. Granular limestone beds and high efficiency cyclones are under study for particulate removal. Acoustical preconditioning of the flue gas is being evaluated as a method to increase the particulate size in order to increase the efficiency of cyclones. Two laser on-line particle size and concentration analyzers have been experimentally evaluated. The use of hot granular bed filters for the removal of gaseous alkali metal compounds is under study. Two sorbents, diatomaceous earth and activated bauxite, have been found to be highly effective for the removal of gaseous NaCl and KCl from hot flue gas.

REDUCING THE ENVIRONMENTAL IMPACT OF
SOLID WASTES FROM A FLUIDIZED-BED COMBUSTOR

Irving Johnson, R. B. Snyder, W. M. Swift and A. A. Jonke

Argonne National Laboratory

The effectiveness of three options for the reduction of the environmental impact of solid sorbents used to control the SO_2 emission from fluidized-bed coal combustion systems will be compared. These options are: (1) pretreatment of the sorbent (use of chemical additives such as NaCl or $CaCl_2$) to increase its reactivity with SO_2, (2) regeneration and reuse of the sorbent, and (3) the use of synthetic sorbents. The quantity of waste generated decreases in the order (1) to (3); the cost increases in the order (1) to (3). The use of chemical additives and the regeneration and reuse of the limestone are viable options. The high cost of synthetic sorbents currently available rule out this option from further consideration.

by

J. S. Halow, U. Grimm, J. S. Mei

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ABSTRACT

A program was initiated late last year at the Morgantown Energy Technology
Center, Department of Energy to demonstrate a 90 percent sulfur retention
capability of an atmospheric fluidized-bed combustor (AFBC) burning a high
sulfur coal. This program was undertaken in response to concerns about the
impact of possible New Source Performance Standards (NSPS) proposed by the
Environmental Protection Agency on the application of AFBC technology. A
high volatile bituminous coal with 4.42 percent sulfur content was selected
for this study. Greer limestone as well as Tymochtee dolomite were used as
sulfur sorbents. Combustion tests were carried out at various operating
conditions to develop AFBC engineering and emissions data on this high sul-
fur coal. Ninety or greater percent of sulfur retention was attained in
nine of the nineteen balance periods. Eighty-five or greater percent sulfur
retention was attained in fourteen of the nineteen balance periods. The
results of the present tests clearly demonstrate that the proposed new stand-
ards for sulfur dioxide emissions can be met by AFBC's.

Fluidized-bed combustion of coal is a process that has been under study since the early 1960's in both England and the United States. This process offers a means of burning a variety of coals and other fuels in an environmentally acceptable manner.

In a fluidized-bed combustor, coal is burned in a bed of inert ash and limestone or dolomite fluidized by the injection of air through the bottom of the bed at controlled rates. The limestone or dolomite in the bed reacts with the sulfur dioxide released by the combustion of the coal, and forms a solid sulfate. Heat is extracted by tubes immersed in the bed and above the bed. Advantages of the AFBC include: Early commercial availability, a projected competitive cost, controllable emissions of SO_x and NO_x, fuel flexibility, and a solid spent sorbent stream that can readily be disposed of along with the coal ash.

At present, New Source Performance Standards (NSPS) limits sulfur dioxide (SO_2), nitrogen oxides (NO_x), and particulate matter that can be emitted from a utility boiler stack. Suppression of SO_2 and NO_x in a fluidized-bed boiler is achieved in the combustion process. The combustion stability provided by the fluidized bed and the balance of heat input and removal from the bed maintains combustion at temperatures below the ash fusion point, and low enough to permit the conversion of limestone and SO_2 to sulfate and to inhibit the formation of nitrogen oxides. To meet NSPS for particulates, conventional mechanical collector and dust removal precipitators or filters will likely be adequate.

This paper discusses SO_2 capture in an AFBC when burning high sulfur coals. Experimental tests burning a high sulfur bituminous coal were conducted in the Morgantown Energy Tecnology Center's 18-inch diameter combustor. This study was undertaken in response to concerns about the impacts of proposed New Source Performance Standards on AFBC technology.

Variables Effecting Sulfur Capture

Sulfur capture is dependent on a number of design and operating variables as well as the sorbent used. A primary variable which can be readily controlled is the calcium to sulfur mole ratio. Increasing the Ca/S mole ratio increases the amount of active sorbent in the bed, thereby increasing sulfur capture. Also of importance is the bed temperature since the SO_2/sorbent reaction is temperature dependent. An optimum sulfur capture temperature of around 1550°F is common for many sorbents. In designing and operating AFBC's, it is desirable to minimize Ca/S mole ratio since high sorbent usage significantly impacts AFBC economics through the cost of sorbent, parasitic heat losses through calcination, and increased spent sorbent disposal costs.

time with the sorbent, and thereby increase sulfur capture. Low velocity also increases gas residence time and, therefore, increases sulfur capture. These variables along with the Ca/S mole ratio need to be balanced to achieve efficient sulfur capture with an economically viable design. Sorbent variety also has a significant effect on sulfur capture.

Reported pilot plant data (1,2,3) has shown sulfur retention results of 90 percent or greater on a variety of fuels and sorbents. Test results reported in this paper provide additional data. Also, since the tests were performed to specifically meet high sulfur capture conditions, the current data allow correlation with operating variables.

Characteristics of Fuel and Sorbents Used in Tests

The coal used in this investigation was a bituminous-A, high volatile coal with a sulfur content of 4.42 percent. It's origin was the Pittswick Coal Company in National, WV, approximately 5 miles south of Morgantown, WV. The company is mining a coal formation better known as the Sweckley seam. The chemical analysis of this coal is given in Table 1.

Table 1
Composition of Pittswick Coal

		Ash analysis %	
Moisture %	0.94		
Ash %	14.04	SiO_2	44.90
Sulfur % Total	4.42	Al_2O_3	22.91
Pyritic	2.36	Fe_2O_3	22.71
Hydrogen %	5.18	CaO	1.06
Total Carbon %	69.45	MgO	0.82
Nitrogen %	1.15	Na_2O	0.28
Oxygen %	4.85	K_2O	2.08
		P_2O_5	0.07
Btu/lb	12,700	TiO_2	1.18
		SO_3	1.00

Table 2
Screen Analysis of Coal

Size Range	1/4 x 0, %	1/8 x 0, %
1/4"-4 mesh	8.1	0.2
4-8 mesh	37.9	8.8
8-16 mesh	21.9	20.7
16-30 mesh	13.5	25.5
30-50 mesh	6.9	17.8
50-100 mesh	3.9	12.1
100-200 mesh	3.0	8.2
200-	4.8	6.8

The sorbents used in the test program were Greer limestone and Tymochtee
dolomite. Greer limestone is the predominant limestone in the area of West
Virginia's high sulfur coals and its sorbtion characteristics can be classi-
fied as good to very good. Tymochtee dolomite was chosen because thermo-
gravimetric analyzer (TGA) studies by the Argonne National Laboratory have
classified this material as one of the best sorbents. It originated in
Huntsville, Ohio, a dolomite formation approximately 50 miles northwest of
Columbus, Ohio. The chemical analysis of both materials are listed in
Table 3. The sorbents were air dried, crushed, and screened before being
fed to the FBC at the top of the expanded bed. The size distributions of
sorbents used in the tests are presented in Table 4.

Table 3
Composition of Sorbents

Elemental Analysis	Tymochtee Dolomite	Greer Limestone
As Carbonates*		
$CaCO_3$%	53.88	86.2
$MgCO_3$%	41.49	5.34
As Oxides*		
CaO%	28.04	44.8
MgO%	19.84	2.15
CO_2%	42.05	47.37

* Balance is moisture, Al_2O_3, SiO_2, and traces.

Size Range	Greer Limestone Wt %		Tymochtee Dolomite Wt%	
	1/4 x 10 mesh	1/4 x 30 mesh	1/4 x 28 mesh	5/10 x 3/32
1/4"-4 mesh	39.8	2.28	0.2	47.87
4-6 mesh	49.9	--	--	--
4-8 mesh	--	34.8	27.7	49.40
6-10 mesh	9.7	--	--	--
8-16 mesh	--	30.34	20.4	1.53
10-12 mesh	0.4	--	--	--
16-30 mesh	--	14.61	17.8	.08
30-50 mesh	--	5.32	10.1	.16
50-100 mesh	--	4.03	6.4	.08
-100	--	8.59	17.4	.88

EXPERIMENTAL FACILITY AND START UP PROCEDURE

The experimental facility at the Morgantown Energy Technology Center for fluidized-bed combustion of low-quality fuel feasibility studies is shown schematically in Figure 1. It is basically a refractory-lined cyclindrical combustor having an internal diameter of 0.46 m (18 inches) in the 1.14 m (45 inches) high bed region with an attached 0.69 m (27 inches) high expanded freeboard section of 0.61 m (24 inches) diameter.

The combustor contains a set of hair-pin-type water cooled heat exchanger tubes located in the bed region and a single pass water cooled heat exchanger in the expanded freeboard. Coal is metered from a hopper and is fed into a fuel injection chamber by a screw feeder. The coal is then injected into the bed near the base of the conical air distributor plate by compressed air. Limestone, when used, is metered from a hopper and fed by a screw feeder directly into the top of the expanded bed. Entrained particulates in the flue gas leaving the combustor are removed by two stages of cyclones followed by bag filters. Particulate matter removed by the primary cyclone is reinjected into the bed for additional carbon burnup. Flue gas leaving the combustor is continuously sampled and analyzed. CO and CO_2 are determined by non-dispersive infra-red analyzers. A chemiluminescence analyzer is used to determine NO and NO_x. SO_2 and total hydrocarbon analyses are made by a flame photometric analyzer and a flame ionization analyzer, respectively, and O_2 by a paramagnetic analyzer.

Start up of the unit is accomplished by preheating the lower part of the combustor to 816°C (1500°F) with premixed natural gas and air. When the desired temperature level is reached, approximately 23 kg (50 lb) of bed

FLUIDIZED BED COMBUSTOR

Labels visible in figure: FUEL, FUEL HOPPER, WEIGH, SCREW, INJECTOR AIR, LIMESTONE, LIMESTONE HOPPER, SCREW FEEDER, COOLING WATER, COOLING WATER, SCREW FEEDER, ASH LOCK HOPPER, COOLING WATER, CYCLONE 1, CYCLONE 2, COMBUSTOR, COOLING WATER, AIR GAS, ASH, INJECTOR AIR, ASH, STACK, BAG FILTERS, ASH, ASH
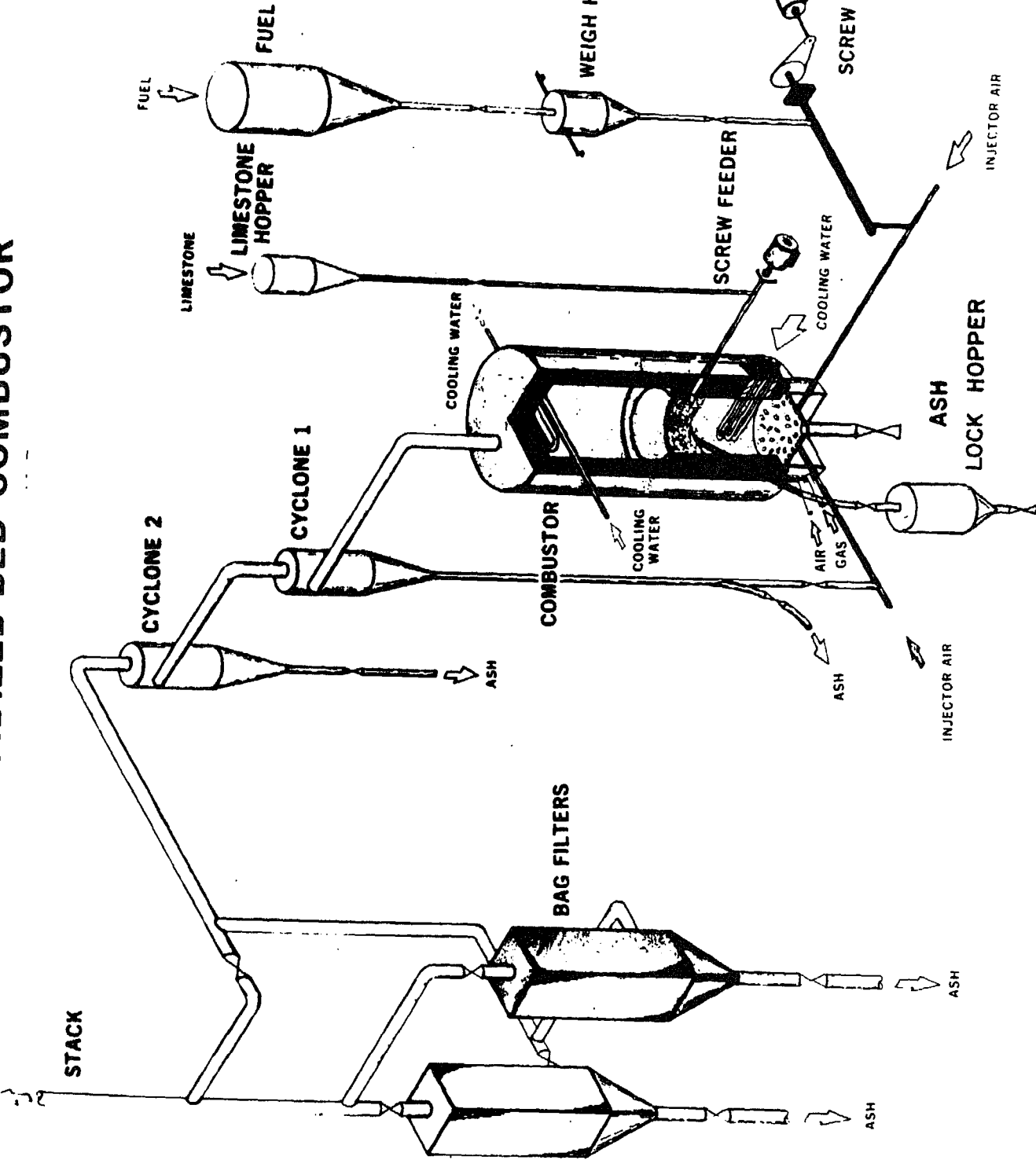
gas is shut off. After desired bed level is attained, fuel combustion is continued with minimum sorbent addition until sulfur dioxide is seen in the flue gas. Then desired operating conditions are established and the unit allowed to stabilize before a data-taking balance period is started. Typical balance periods are 10 hours in duration.

RESULTS OF SULFUR RETENTION STUDIES

It has been mentioned previously that the present study was undertaken in response to the concern about the impact of the proposed NSPS of 90 percent sulfur retention on AFBC technology. The studies, therefore, were carried out at conditions which could lead to high sulfur retention in the bed. The variables investigated for the present study have been Ca/S mole ratio, fluidized-bed temperature, gas residence time, type and particle size of sorbent. Table 5 presents a summary of the experimental conditions and the sulfur retention results for the experiments carried out in this study. The analysis of the results are discussed below.

Figure 2 illustrates the effect of average bed temperature on the percentage of sulfur captured by two different types of sorbent, Greer limestone and Tymochtee dolomite. Data for Greer Limestone show a clear temperature dependence (solid curve) in spite of variations Ca/S ratio, gas residence time and sorbent particle size. A maximum reactivity around 1550°F is evident. Tymochtee Dolomite does not show a clear trend in this data. An optimum temperature range for sulfur capture is observed for Greer limestone between 1500° to 1600°F. As seen, 90 percent or better sulfur retention can be obtained over the optimum temperature range.

The effect of Ca/S mole ratio on sulfur retention is shown in Figure 3 for the two sorbents at a bed temperature range between 1500° to 1600°F where sulfur capture had been optimized. The present results indicate that for this particular high sulfur coal and Greer limestone, a calcium-to-sulfur mole ratio of 2.0 would be adequate to assure compliance with the proposed NSPS of 90 percent sulfur removal. With Tymochtee Dolomite, a Ca/S ratio of 1.5 appears to be adequate to meet a 90% sulfur retention with the revised NSPS of 85 percent sulfur retention, lower Ca/S ratios would appear to be sufficient in the optimum bed temperature range and with the 0.75 sec to 1.00 sec residence times used in these tests, but the data is insufficient to draw a firm conclusion at this retention level. The calcium-to-sulfur ratio required to maintain 90 percent sulfur removal, however, is lower than the projected value (Ca/S $\cong$ 2.8) by Westinghouse kinetic model (4) and by the MIT model (Ca/S $\cong$ 3.1) (5) at similar operating conditions.

TABLE 5.   SUMMARY OF EXPERIMENTAL CONDITIONS AND SULFUR RETENTION RESULTS

| Run No.	Sorbent Type	Particle Size (Sorbent)	Particle Size (Coal)	Bed Temp. (°F)	Superfic. Velocity (ft/sec)	Bed Depth (ft)	Resid. Time (sec)	Ca/S Mole (ratio)	SO_2 Emission (ppm)	SO_2 Emission (lb/10^6 Btu)	Sul. Dete...
1/1	G. Lime.	1/4"x10 mesh	1/4x0"	1524	2.99	3.00	1.00	3.91	240	0.54	92.
1/2	G. Lime.	1/4"x30 mesh	1/4x0"	1470	2.91	3.00	1.03	2.62	646	1.42	80.
1/3	G. Lime.	1/4"x30 mesh	1/4x0"	1533	3.03	3.00	0.99	3.44	255	0.62	91.
1/4	G. Lime.	1/4"x30 mesh	14/x0"	1536	3.45	3.00	0.87	2.05	259	0.63	91.
1/5	G. Lime	1/4"x10 mesh	1/4x0"	1582	3.51	3.00	0.85	1.82	344	0.56	92.
1/6	T. Dolom.	1/4"x28 mesh	1/4x0"	1465	3.43	3.00	0.87	1.21	900	1.67	77.
1/7	T. Dolom.	1/4"x28 mesh	1/4x0"	1444	3.39	3.00	0.88	1.24	300	0.59	92.
1/8	T. Dolom.	1/4"x28 mesh	1/8x0"	1546	3.51	3.00	0.85	0.80	855	1.44	80.
1/9	T. Dolom.	5/16"x3/32"	1/8x0"	1547	3.51	3.00	0.85	1.20	412	0.75	89.
1/10	T. Dolom.	5/16"x3/32"	1/8x0"	1556	3.82	3.00	0.79	1.43	439	0.96	86.
1/11	T. Dolom.	5/16"x3/32"	1/8x0"	1554	3.95	3.00	0.76	1.44	303	0.57	
2/1	G. Lime.	1/4"x10 mesh	1/4x0"	1653	3.51	3.00	0.85	2.67	414	0.76	89.
2/2	G. Lime.	1/4"x10 mesh	1/4x0"	1507	3.27	3.00	0.92	1.87	112	0.19	97.
2/3	G. Lime.	1/4"x10 mesh	1/4x0"	1463	3.13	3.00	0.96	2.13	1427	2.78	60.
2/4	G. Lime.	1/4"x10 mesh	1/4x0"	1670	3.50	3.00	0.86	2.82	493	0.88	87.
2/4R	G. Lime.	1/4'x10 mesh	1/4x0"	1637	3.58	3.00	0.84	2.68	650	1.10	84.
2/5	G. Lime.	1/4"x10 mesh	1/4x0"	1555	3.44	3.00	0.87	2.99	155	0.31	95.
2/6	G. Lime.	1/4"x10 mesh	1/4x0"	1482	3.30	3.00	0.91	4.21	471	1.03	85.
2/7	G. Lime.	1/4"x10 mesh	1/4x0"	1562	3.42	3.00	0.88	3.91	152	0.39	94.
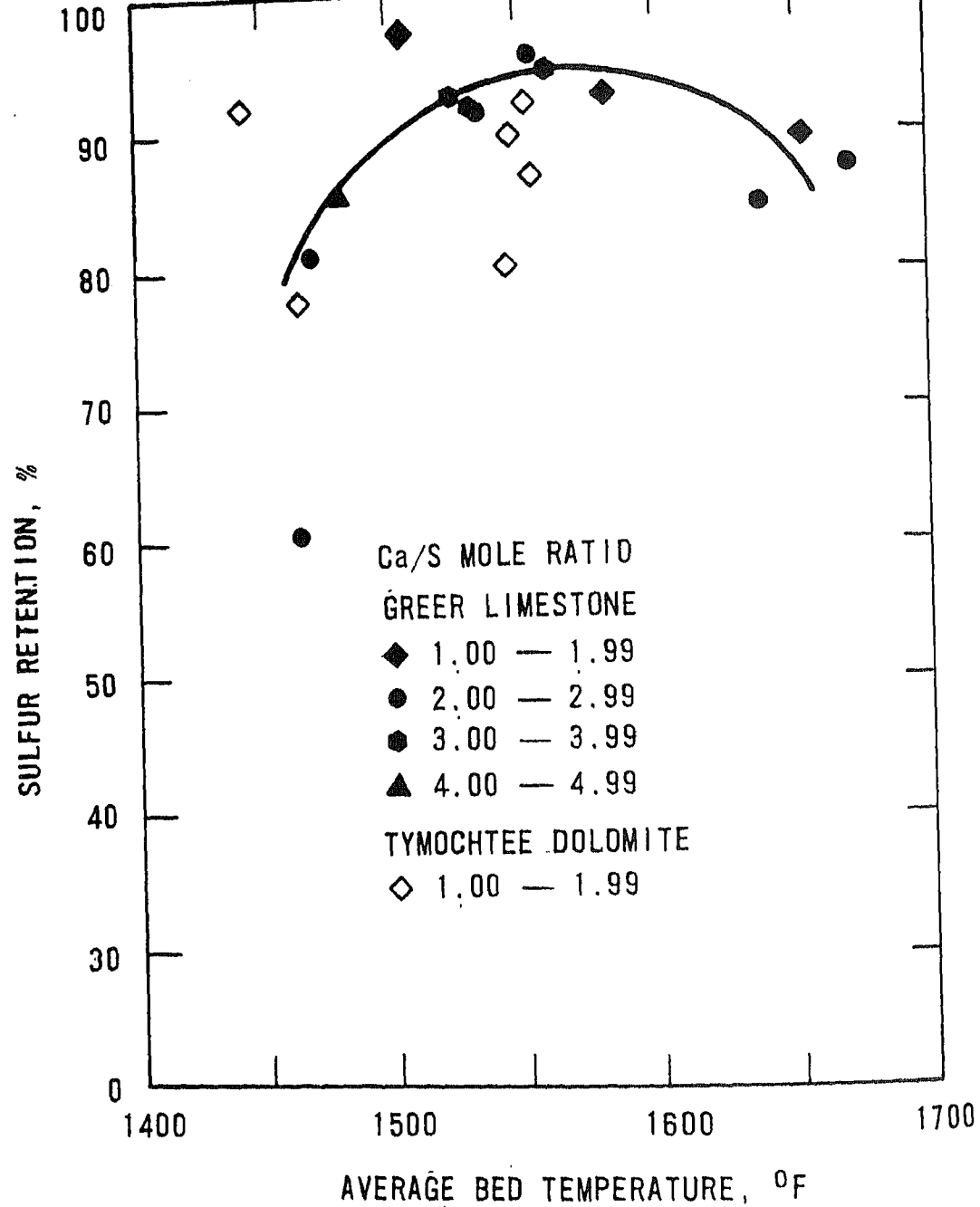
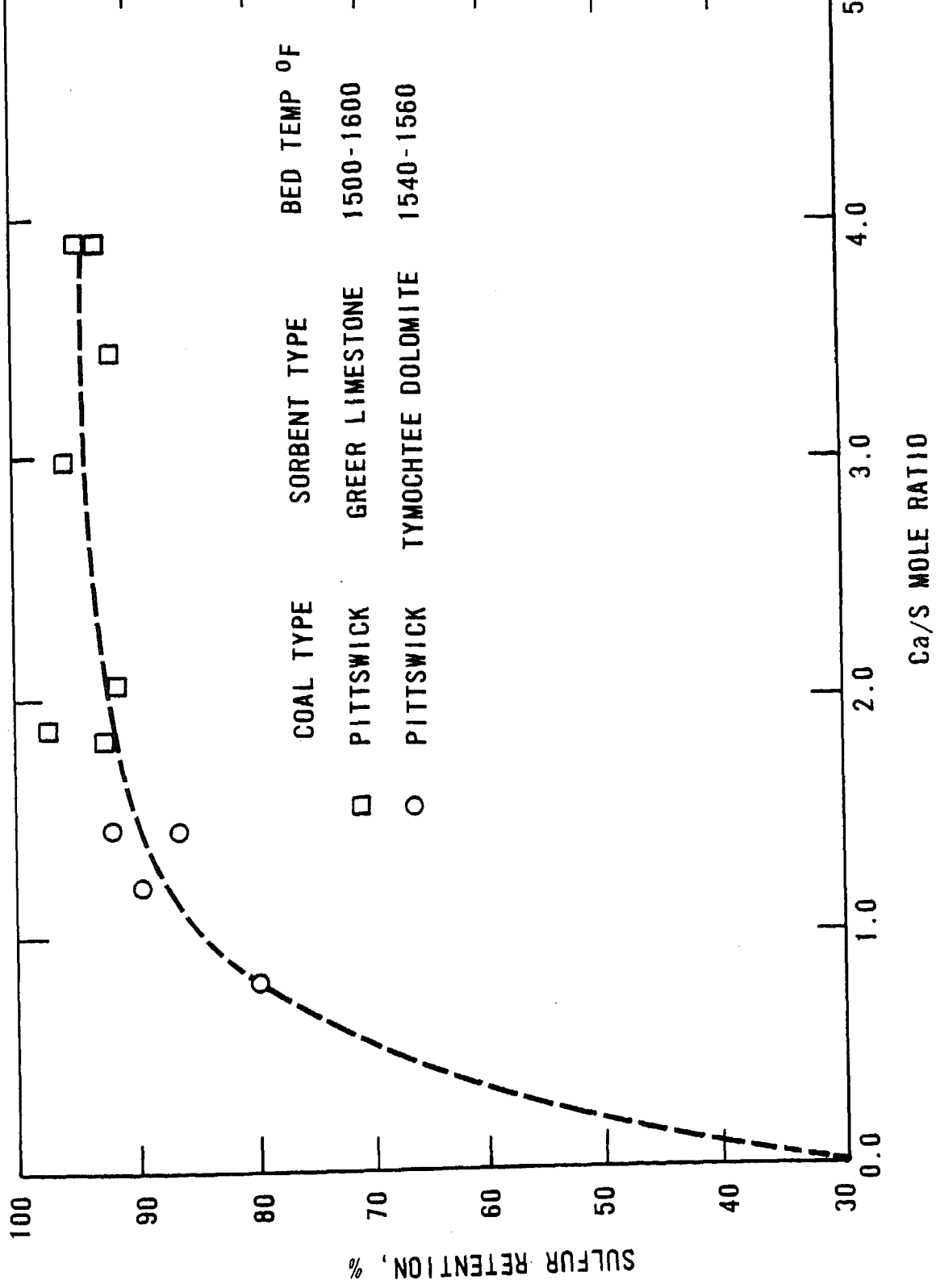FIGURE 2. Effect of Average Bed Temperature on Sulfur Retention

FIGURE 3. Effect of Ca/S Mole Ratio on Sulfur Retention

Greer Limestone follow a single curve which decreases with increasing Ca/S mole ratio. At high Ca/S mole ratio sorbent residence time in the bed is shortened loading to lower utilization. Variations in particle size, gas residence time, and temperature were relatively small in the studies. These conditions results, in terms of utilization, in very little scatter in the data in Figure 4.

COMPARISON OF EXPERIMENTAL AND PREDICTED CALCIUM UTILIZATION

Calcium utilization of a given limestone can be related to the calcium-to-sulfur molar ratio and sulfur retention as stated by the following equation.

$$u = \frac{R}{Ca/S} \tag{1}$$

where   u = mole fraction of calcium converted to calcium sulfate
        R = fraction of sulfur dioxide retained
   Ca/S = calcium to sulfur molar feed ratio

A kinetic model for SO_2 capture developed by Keairns, et al., (6) was used to predict the calcium utilization of Greer limestone and Tymochtee dolomite. This model requires the use of the thermogravimetric analyzer (TGA) kinetic data together with a derived fluidized-bed desulfurization equation. This model assumes uniform SO_2 generation within the fluid bed.

$$u = \frac{1}{Ca/S} \left[1 - \frac{V}{kH\varepsilon} \left(1 - e^{-\frac{kH\varepsilon}{V}} \right) \right] \tag{2}$$

where V = superficial gas velocity
     H = expanded bed height
     ε = bed voidage
     k = average reaction rate constant

For a given set of operating conditions, Equation 2 gives the calcium utilization as a function of an average reaction rate constant, k. This constant is a measure of the reactivity of the sorbent bed. Reactivity can be measured independently by the TGA technique and is found to depend on type of sorbent, sorbent particle size, temperature, gas pressure, gas composition, calcining conditions as well as the sorbent utilization. As utilization increases, the reactivity of the remaining calcium in the sorbent decreases loading to a lower reaction rate constant. TGA data provides a measure of this constant as a function of utilization for a fixed set of bed conditions. Combining
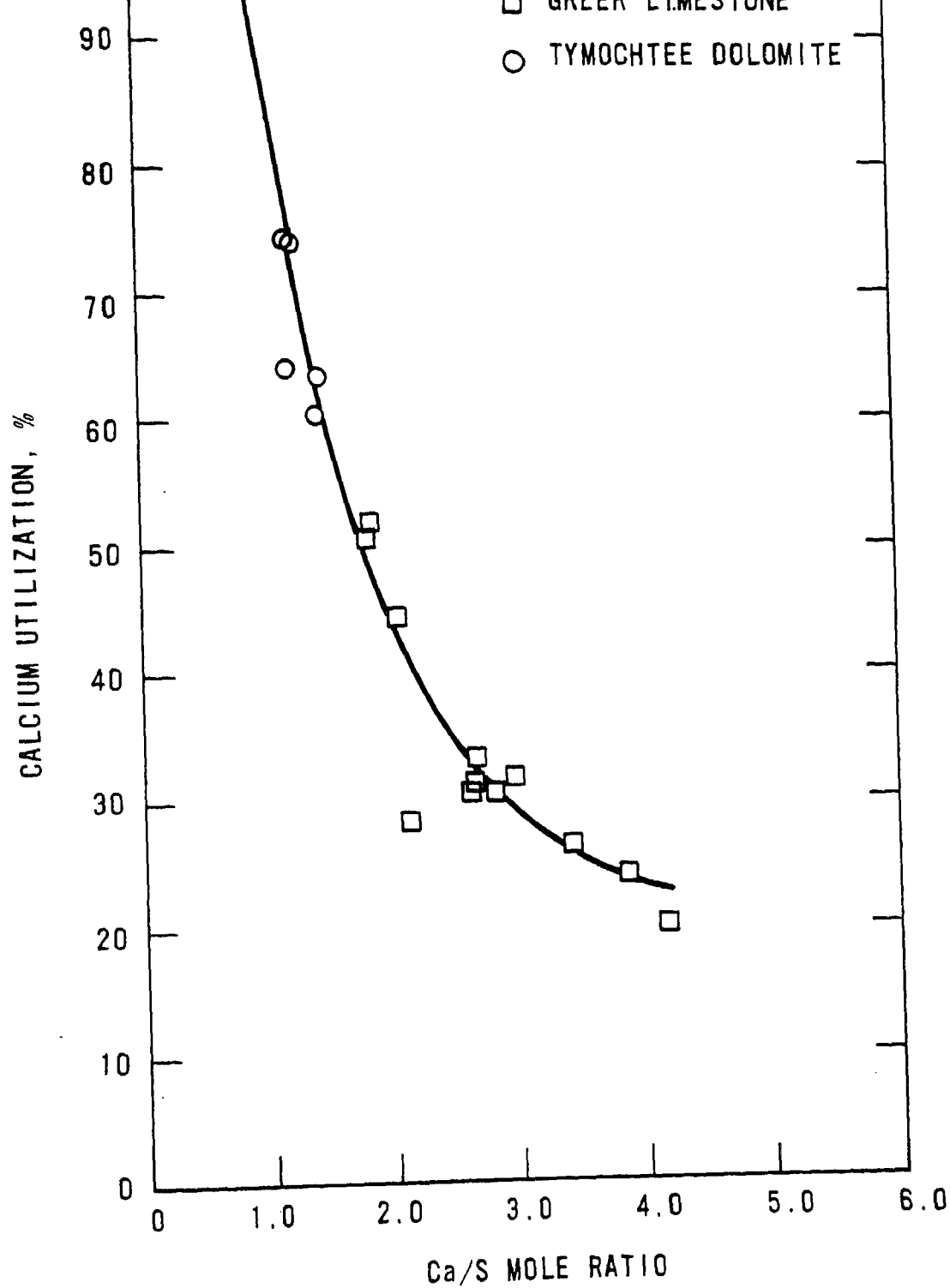
FIGURE 4. Calcium Utilization vs. Ca/S Mole Ratio

A comparison of predicted and experimental utilization is given in Figure 5. The TGA data (7) used to develop the predicted utilizations was obtained under the following conditions: precalcined in 20% CO_2 at 1650°F and then reacted with a 0.3% SO_2 - 5% O_2 - N_2 synthetic sulfation gas. As seen, the predicted calcium utilization for both sorbents by the Westinghouse model is in good agreement with the test data, although slightly higher than the experimental results. An explanation for this discrepancy is due to the fact that the TGA data were obtained from a smaller sorbent particle size. Comparison of predicted and measured percent sulfur retention are far less satisfactory, however, with predicted retentions being consistently higher than measured retentions. This discrepancy indicates the sensitivity of the model to TGA conditions, especially at high sulfur retention levels.
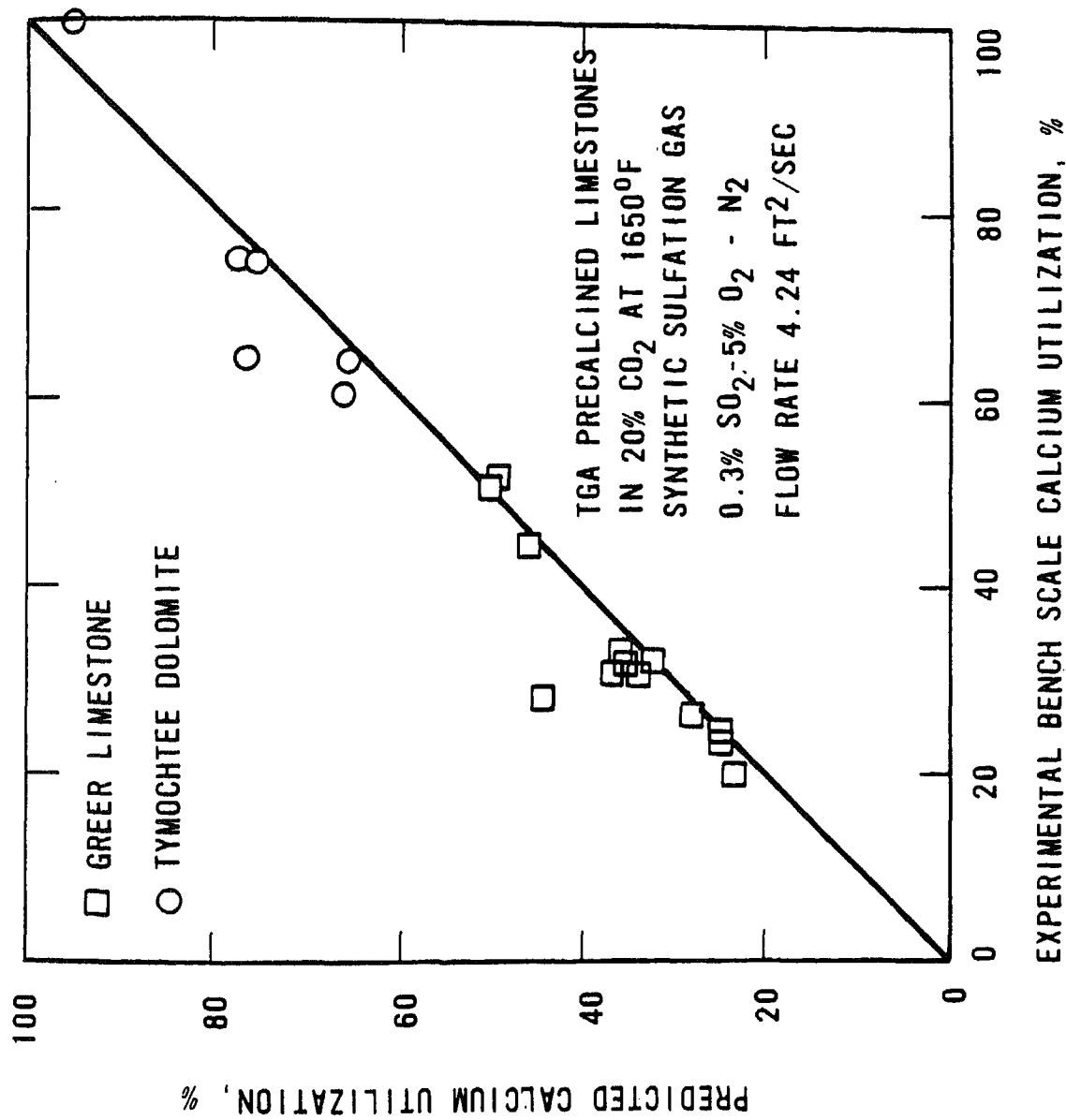
FIGURE 5. Comparison of Predicted and Fluidized Bed Calcium Utilization

Based on the combustion tests with a high sulfur coal (4.42 wt %) and two different types of sorbents, the following conclusions can be drawn:

(1) An optimum temperature range between 1500°-1600°F for sulfur capture was observed for the Pittswick coal and Greer limestone.

(2) The 90 percent sulfur removal is attainable with a Ca/S mole ratio close to or greater than 2.0 for Greer limestone when bed temperature is maintained in the 1500-1600°F range and residence times in the 0.75-1.0 second range.

(3) Revised NSPS 85 percent sulfur retention requirement can likely be met with a Ca/S mole ratio less than two, provided bed temperature is maintained between 1500°-1600°F and gas residence time is at least 075-1.0 seconds.

(4) The predicted calcium utilization for both sorbents by the Westinghouse model is in good agreement with the combustion test data. Retention predicted by this model is sensitive to careful matching of TGA conditions and did not provide satisfactory agreement with experimental results.

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Warren W. Bunker
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INTRODUCTION

One of the objectives of the Fossil Fuel Utilization Division of the
Department of Energy is to encourage increased coal usage in base load
electrical generation power plants. Studies indicate that one of the
more attractive approaches in this regard is the integrated gas turbine
combined cycle. In support of this objective we then have the task of
developing the technologies required to burn coal in utility size gas
turbines in an environmentally acceptable manner.

There are three methods of burning coal in a gas turbine: (a) directly,
as in a pressurized fluidized bed combustor; (b) as a gas; and (c) as a
liquid derived from coal. It is the combustion of coal as a gas and as
a liquid that we will discuss.

The gas turbine visualized in the program is to be a major component of
a combined cycle plant. A diagram of such a plant, designed to burn low
Btu gas, is shown in Figure 1. The combined cycle portion consists of
the gas turbine which exhausts into a heat recovery boiler which, in turn,
generates steam for the steam turbine bottoming cycle. This combined
cycle may be integrated with an air blown low Btu gasifier, 150 Btu/cu.
ft. as illustrated in Figure 1, or the gasifier could be oxygen blown
which would result in the generation of a medium Btu gas, 300 Btu/cu.
ft. If the gasifier is oxygen blown, the oxygen would be generated by
means of an on-site air separation plant. Of course should a coal-
derived liquid be the fuel, the gasifier system shown would be replaced
by an off-site coal liquefaction plant.

In summary, the fuels available for combustion in a gas turbine combined
cycle power plant are low and medium Btu gases as well as residual and
coal-derived liquids. The reason that residual oil comes under considera-
tion is two fold. First, residuals and coal-derived liquids have a common
emission problem - fuel bound nitrogen which is an additional source of
NO_x from the combustion process. Secondly, it is possible that residual
fuels may be burned in place of distillate fuels prior to coal-derived
fuels being available in sufficient quantities. DOE programs have combined
residual and coal liquids together as heavy liquids.

levels for various fuels plotted against combustor exit temperatures. The plot shows only trends since each manufacturer would have different results depending on the combustor design. The NO_x levels represent thermal NO_x only and assume no entrained nitrogen. As shown, medium Btu gas represents the highest NO_x output. This is due to the higher hydrogen content which results in a higher stoichiometric temperature. Low Btu gas, on the other hand, is the lowest NO_x generator, how low depends on the gas constituents. The NO_x levels of residual fuel will be in the general neighborhood of the No.2 oil. As you can see, all fuels except low Btu gas exceed the proposed EPA standards of 75PP at combustor exit temperatures greater than 1900F.

A SOLUTION

One solution to the problem is the use of catalytic combustors in gas turbines. Figure 3 is a simplified explanation of why the NO_x level is drastically reduced when such combustors are used. The illustration at the top shows a conventional combustor operating at its most efficient point under near stoichiometric conditions. The high gas temperature is reduced to the required turbine inlet temperature by means of dilution air. On the bottom chart we have plotted gas temperature versus the axial distance along the combustor. The curve shows that the temperature climbs to over 4000F during the burning process. The catalytic combustor is shown in the center of Figure 3. In this type the fuel is mixed with air and introduced into the catalytic reactor where it burns under lean conditions. As shown in the bottom diagram the gas temperature gradually builds up to the turbine inlet temperature thus staying below 3000F. The significance of the 3000F level is that thermal NO_x generation is generally produced at gas temperatures in excess of 3000F. Therefore, a combustion process which maintains a gas temperature below 3000F will produce little or no thermal NO_x.

In order to produce the large catalytic surface required, a catalytic reactor is made of high temperature ceramic material with a honeycomb structure. Figure 4 illustrates a typical reactor cross section in which a cell structure is produced by a sine wave ceramic element.

The design problem then involves balancing the surface area required with the pressure drop incurred. Figure 5 illustrates the performance of a typical reactor designed for low Btu gas. The design point indicates an efficiency of 99.8% at a pressure drop of 5% and a gas velocity of 100 ft. per second.

turbine manufacturers, there are several organizations who are supporting catalytic combustor technology programs. These are: The Department of Energy (DOE), the Environmental Protection Agency (EPA), the Electric Power Research Institute (EPRI) and the National Aeronautics and Space Administration (NASA).

EPA was one of the first to explore the possibilities of this technology and they are continuing work on a broad field ranging from home heating to utility boilers. EPRI has recently entered the field and they are interested in gas turbine applications especially in the development of retrofit combustors for turbines burning clean fuels located in areas with strict environmental restrictions such as Southern California. NASA is doing work for DOD to develop catalytic combustors for aircraft use and for DOE originally in the automotive gas turbine area, now they are working in the utility gas turbine field.

DOE's interest in catalytic combustion is in support of the coal burning gas turbine. Presently we have two programs with Engelhard Industries, a leading catalyst manufacturer, involving the investigation of the burning of coal-derived gases in a laboratory test facility. The programs started with an investigation of low Btu gas and has been expanded to include medium Btu gas. Both programs involve the burning of a simulated gas in a laboratory test rig.

In addition to this work, we have initiated a program with NASA involving the catalytic combustion of heavy liquids. The objective of the program is to investigate the effect on combustion of fuel droplet size. We are exposing a catalytic combustor to various droplet sizes from a fully vaporized condition to a fine and a coarse spray and measuring differences in performance. The program will be accomplished partly in NASA test facilities and with the help of outside contractors hopefully gas turbine manufacturers.

With regard to results so far, the laboratory test work indicated that a low or medium Btu, utility size, integrated gasifier combined cycle power plant can be built to have near zero NO_x emissions, through the use of catalytic combustors. In addition, such a plant would have a clear stack and a sulfur level below EPA limits. This would be very close to an ideal environmentally acceptable power plant.

As far as future plans are concerned of course we must complete the heavy liquid combustor tests previously described. In addition, we are making plans for the next phase of this program which would involve more testing and the design of a gas turbine combustor, its fabrication, rig testing, and eventual inclusion in a gas turbine for field testing.
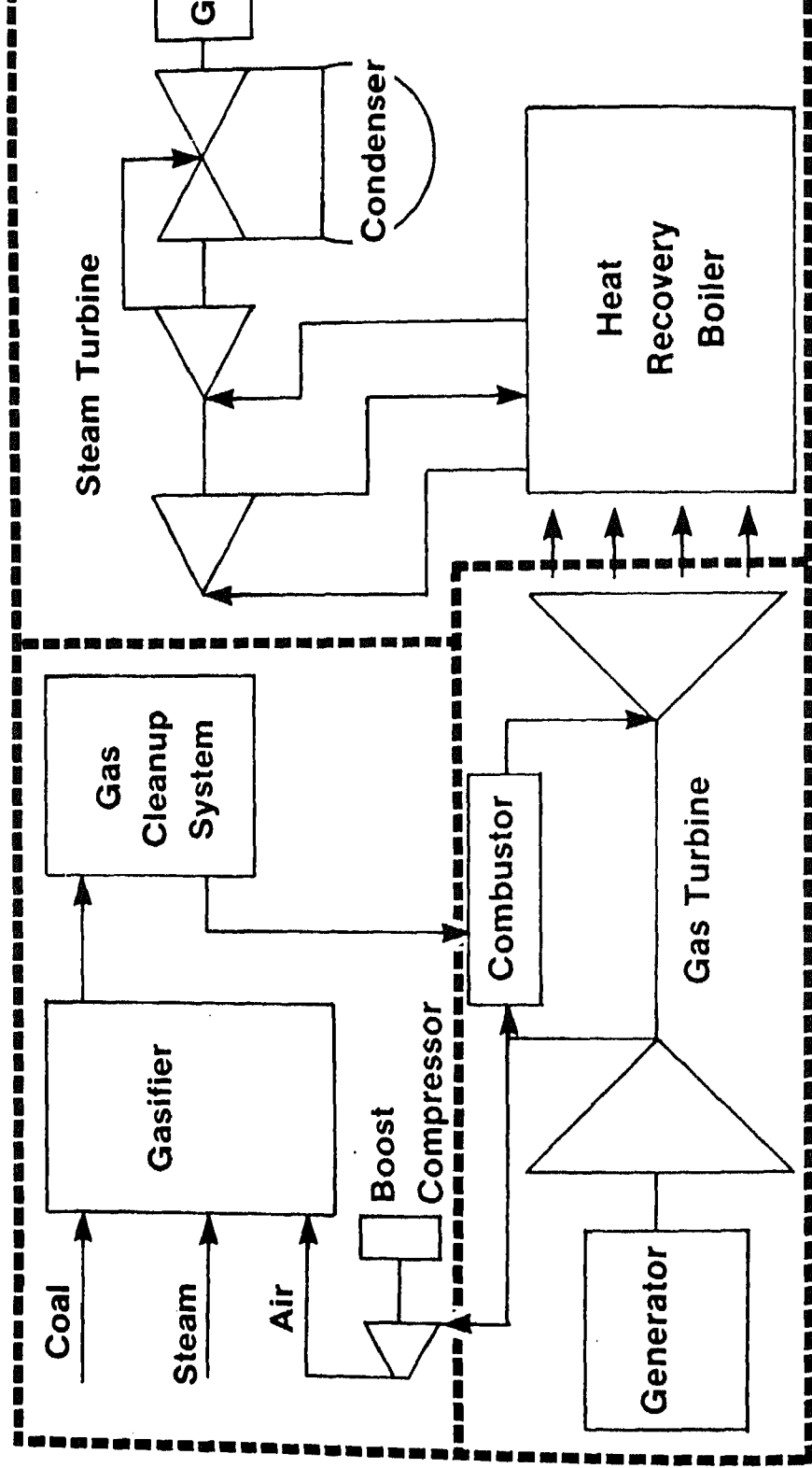
HTTT Program

Typical Combined Cycle For Low BTU Gas

FIGURE 1

FIGURE 2

Dilution Air

Catalytic Reactor

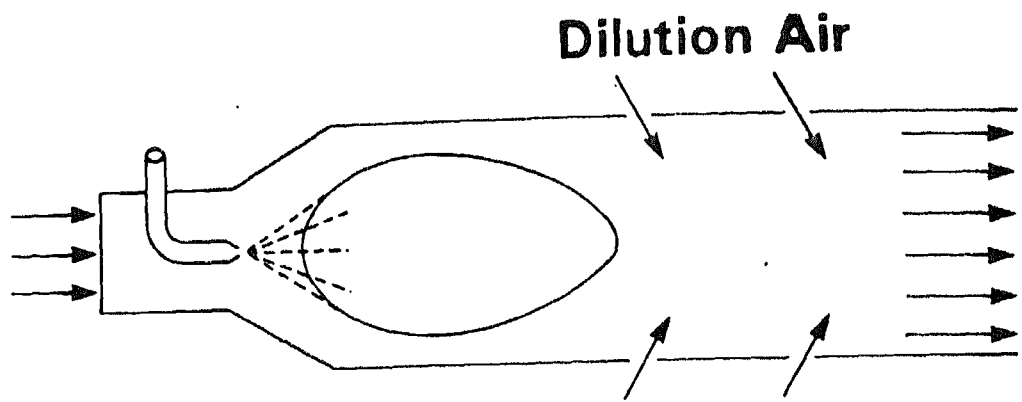Fuel Presentation

Conventional
Combustion

3000 F

Temperature
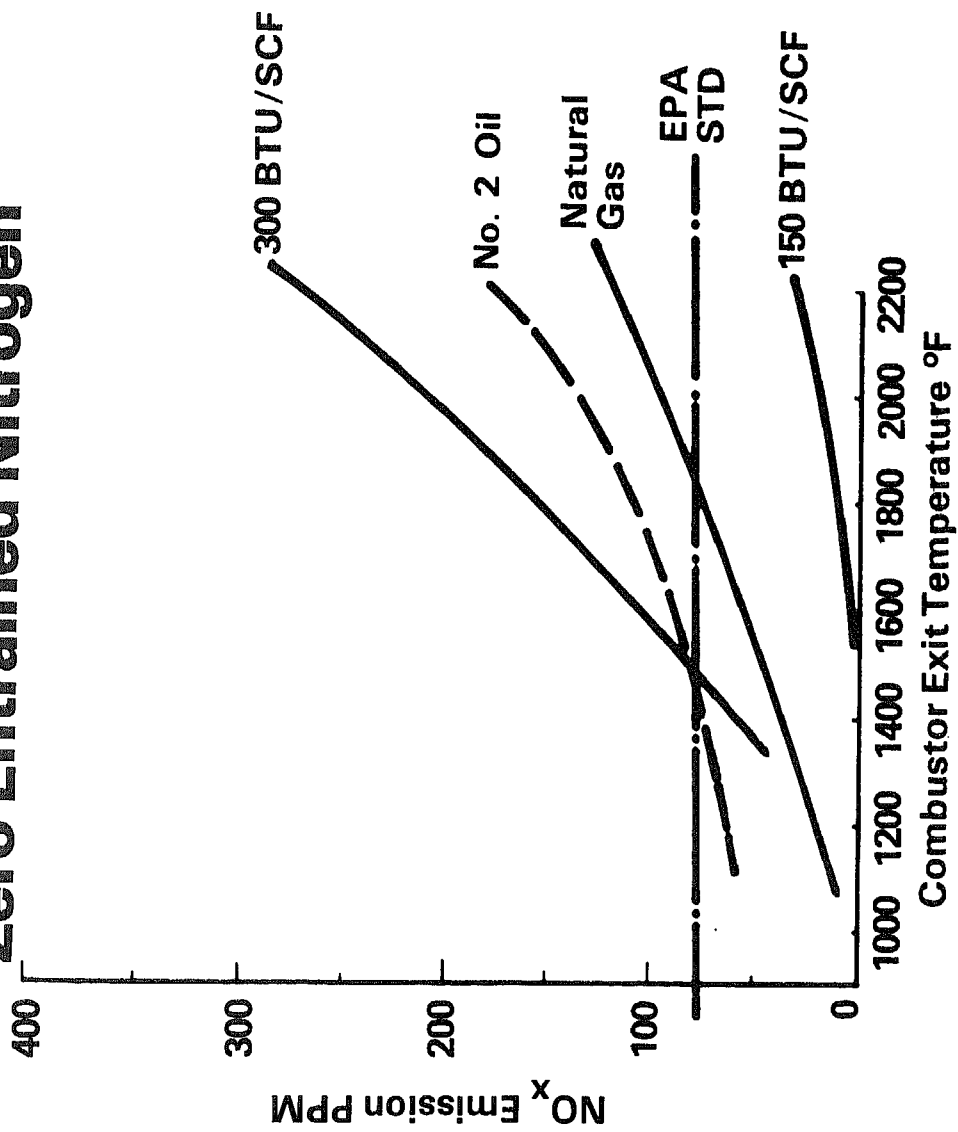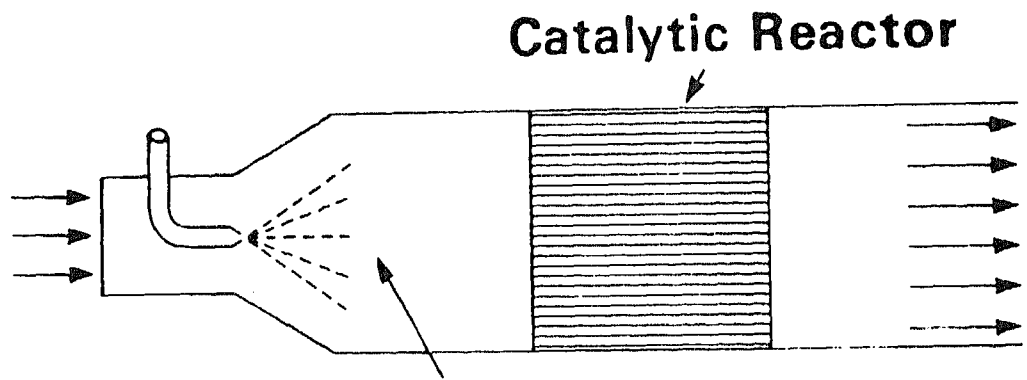
Catalytic
Combustion
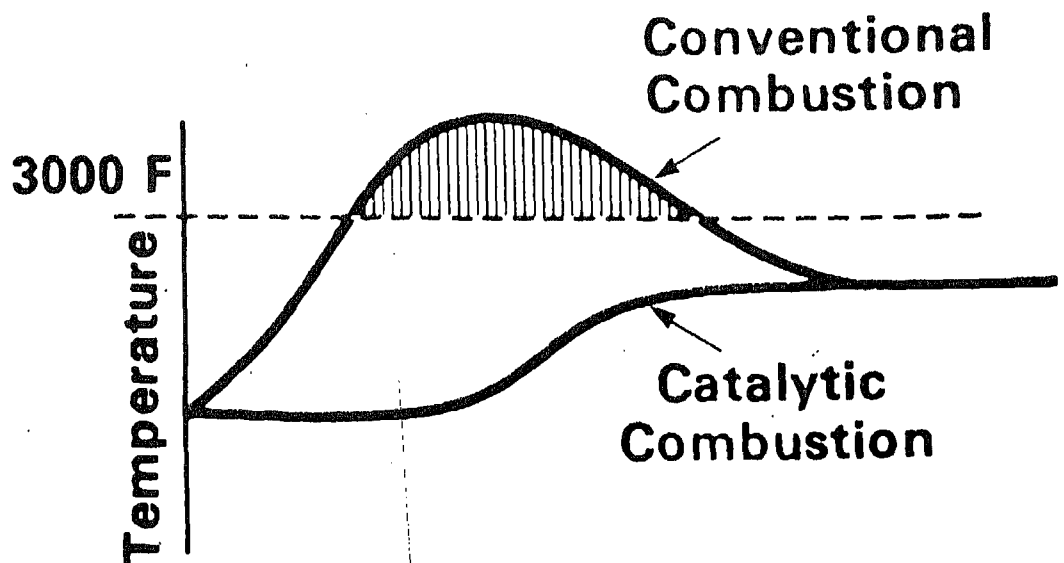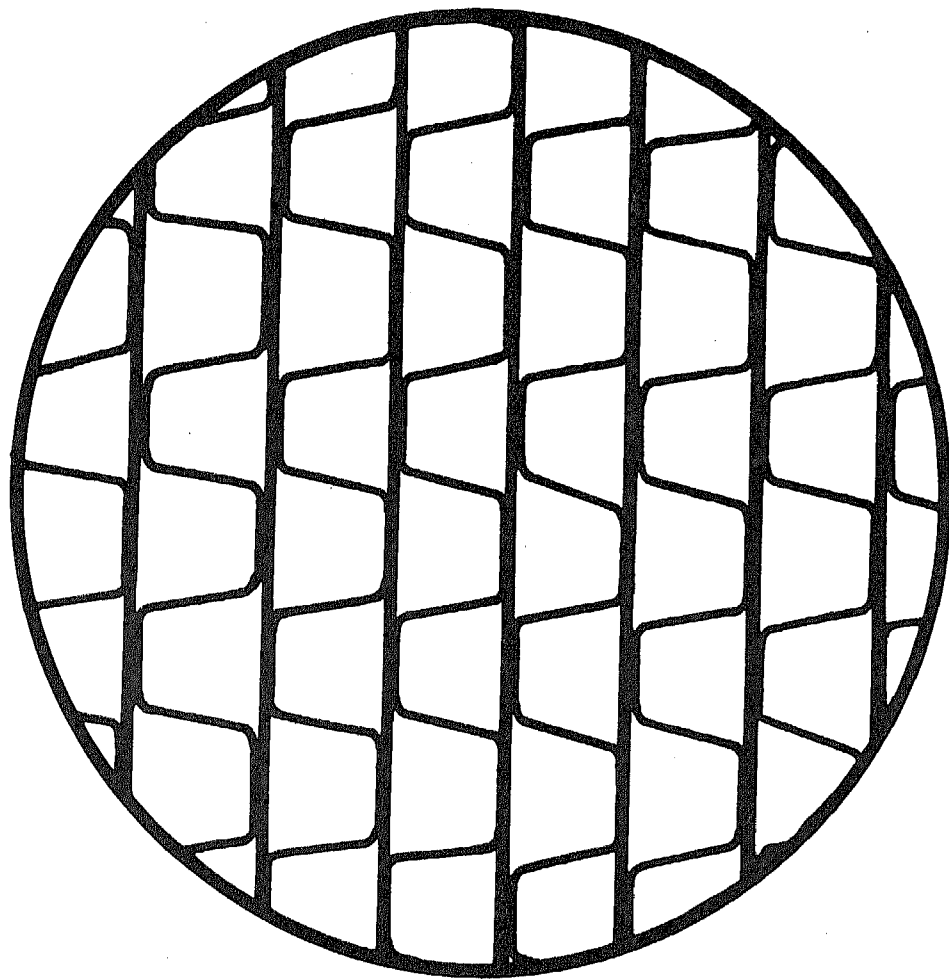
FIGURE 3

Catalytic Reactor Cross-Section

FIGURE 4

Catalytic Combustor Performance on Low BTU Gas

Combustion Efficiency — Percent

Pres Drop — 5%

Reference Velocity — FT/SEC

THE GRAND FORKS ENERGY TECHNOLOGY CENTER

Gerald M. Goblirsch and Harvey M. Ness
DOE, Grand Forks Energy Technology Center
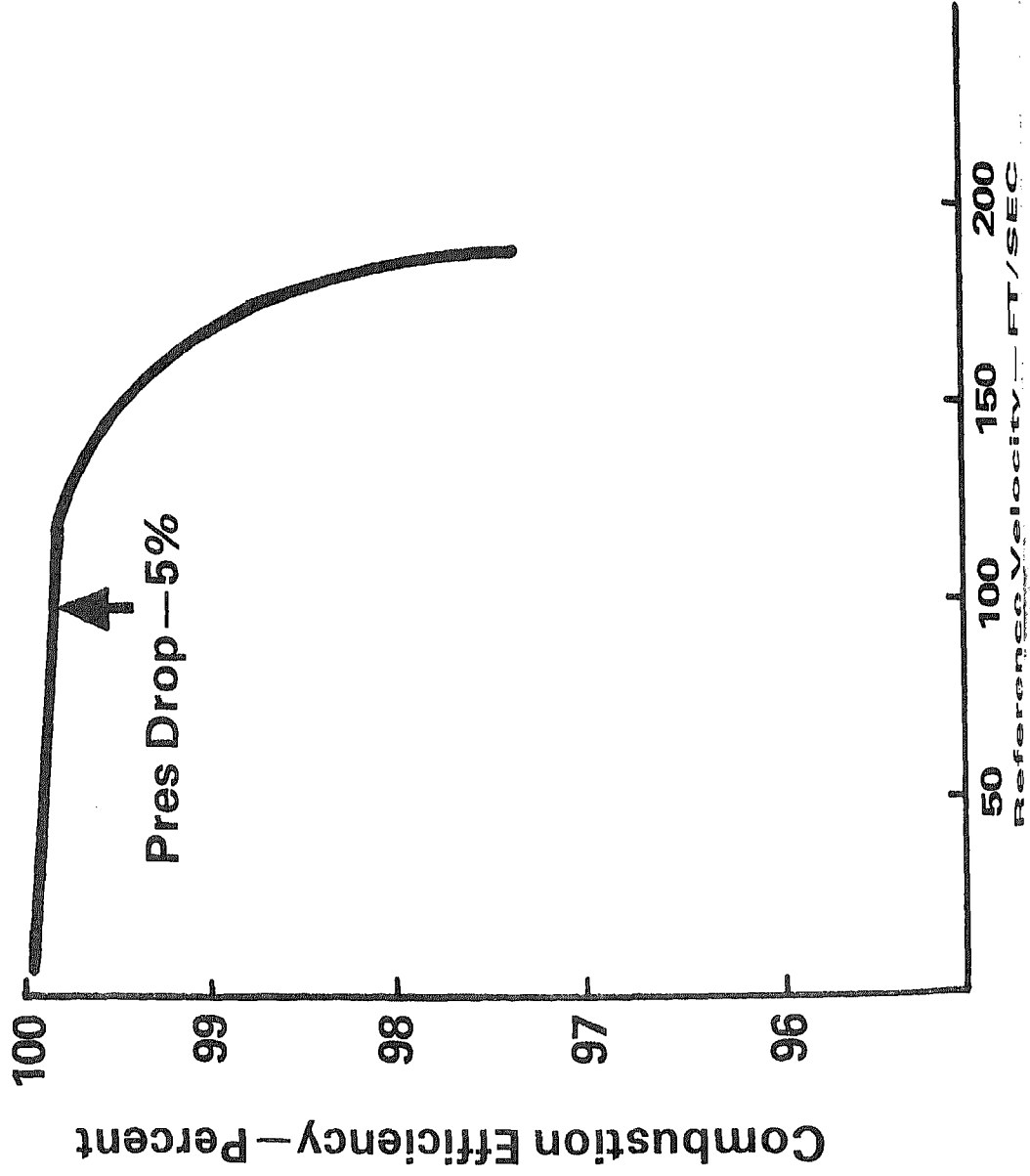
1. INTRODUCTION

Several important advantages of atmospheric fluidized-bed combustion (AFBC) over conventional coal combustion systems are: 1) lower emissions of sulfur dioxide (SO_2); 2) lower concentrations of the oxides of nitrogen (NO_x) in the flue gases; 3) higher heat transfer coefficents; and 4) the ability to utilize fuels of varying quality.

The lower combustion temperatures encountered during AFBC are responsible for the lower flue gas pollutant emissions of SO_2 and NO_x. The low temperatures limit the thermal fixation of atmospheric nitrogen in the AFBC process and, in general, the emissions of NO_x are below the level expected if all the fuel-bound nitrogen would be converted to NO_x. This is probably a result of the low equilibrium concentration of NO at low combustion temperatures, and the chemical reduction by other species in the flue gas. The lower temperatures also enhance the absorption of sulfur dioxide by sorbent materials in the fluidized bed. At the lower temperatures the equilibrium favors the formation of solid alkali sulfates and the lack of sorbent blinding by fusion of the ash constituents.

Heat transfer surfaces in the AFBC may be inserted directly in the bed where the heat transfer coefficient will be substantially higher than the combined convective radiative coefficient occurring in conventional systems. This higher heat transfer coefficient would result in a much smaller physical unit for AFBC than conventional systems of similar power outputs. The AFBC's ability to operate on a wide variety of fuels of varying quality is partly due to the very high heat transfer rates to the fuel particle or droplet.

Western low-rank coals and lignites are especially well suited to AFBC because of the high inherent levels of ash alkali such as calcium, magnesium, and sodium which will absorb some of the sulfur dioxide generated by from the combustion of the coal sulfur (1). The absorption of sulfur dioxide by Western coal ash alkali represents an advantage over Eastern coals since far less limestone would be required to control SO_2 emissions, resulting in lower limestone requirements, less heat loss due to calcination, and less solid waste for disposal. Additionally, many Western coals containing high levels of sodium cause severe boiler tube fouling in conventional power generation systems (2). The AFBC may be able to burn these coals, and other low-quality fuels, without the fouling problems.

Low-rank Western coals are highly reactive, and it is possible that they will have higher combustion efficiencies in AFBC than Eastern coals (3). The high inherent alkali in Western low-rank coals would allow these coals

This report presents results of experiments conducted on a 6-inch fluidized-bed combustor at GFETC. The experiments were conducted on 11 low-rank Western coals. Data are presented on particulate emission characterizations, bed material agglomeration, nitrogen oxide emissions, and on sulfur retention as a function of bed temperature, inherent alkali-to-sulfur ratio, and fluidizing velocity.

2. EQUIPMENT AND OPERATING PROCEDURES

Experimental Equipment

A schematic of the 6-inch AFBC used in these studies is shown in figure 1. The combustor shell is constructed of 6-inch, type 316, schedule 40 stainless steel pipe. The shell is 10 feet high, which allows sufficient freeboard above the bed to limit elutriation. The combustor shell is enclosed by a stainless steel sheet-metal skin which is filled with insulation. Internal stainless steel cooling coils provide the primary means for controlling bed temperature. Water flow through the cooling coils is controlled manually using valves and rotometers. Combustion air supplied by a 7.5 hp positive displacement-type blower is electrically preheated to provide pre-heating of the bed for ignition, and to maintain a selected air preheat temperature during a combustion run. The combustion air is measured by the use of a flat plate-type orifice with flange taps.

Coal is metered to a pneumatic coal injector by a volumetric screw-type feeder. The rate of coal injection can be varied from about 10 lb/hr to 40 lb/hr. The off-gases from the combustor are cooled by a series of heat exchangers to about 400° F. Particulate is removed from the gas stream by primary and secondary cyclones, and a fiber filter before entering the induced draft fan. The induced draft fan is also used to control combustor static pressure. The fly ash collected in the primary cyclone may be reinjected directly to the fluidized bed by the use of a pneumatic injector, shown by the dotted line in figure 1. Flue gases are sampled during each test for total particulate, both upstream and downstream of the cyclone separators. The flue gas sample stream is cleaned of particulate by a small cyclone and a filter, followed by moisture removal using a refrigerated conditioner. The stack gases are continuously monitored during a combustion run for oxygen, carbon dioxide, carbon monoxide, nitric oxide, and sulfur dioxide. Oxygen concentrations are determined by an amperometric-type analyzer. Carbon monoxide and carbon dioxide concentrations are monitored by infrared analyzers. Nitric oxide emissions are analyzed by a chemiluminescent-type analyzer, and the sulfur dioxide concentrations are monitored using an ultraviolet analyzer.
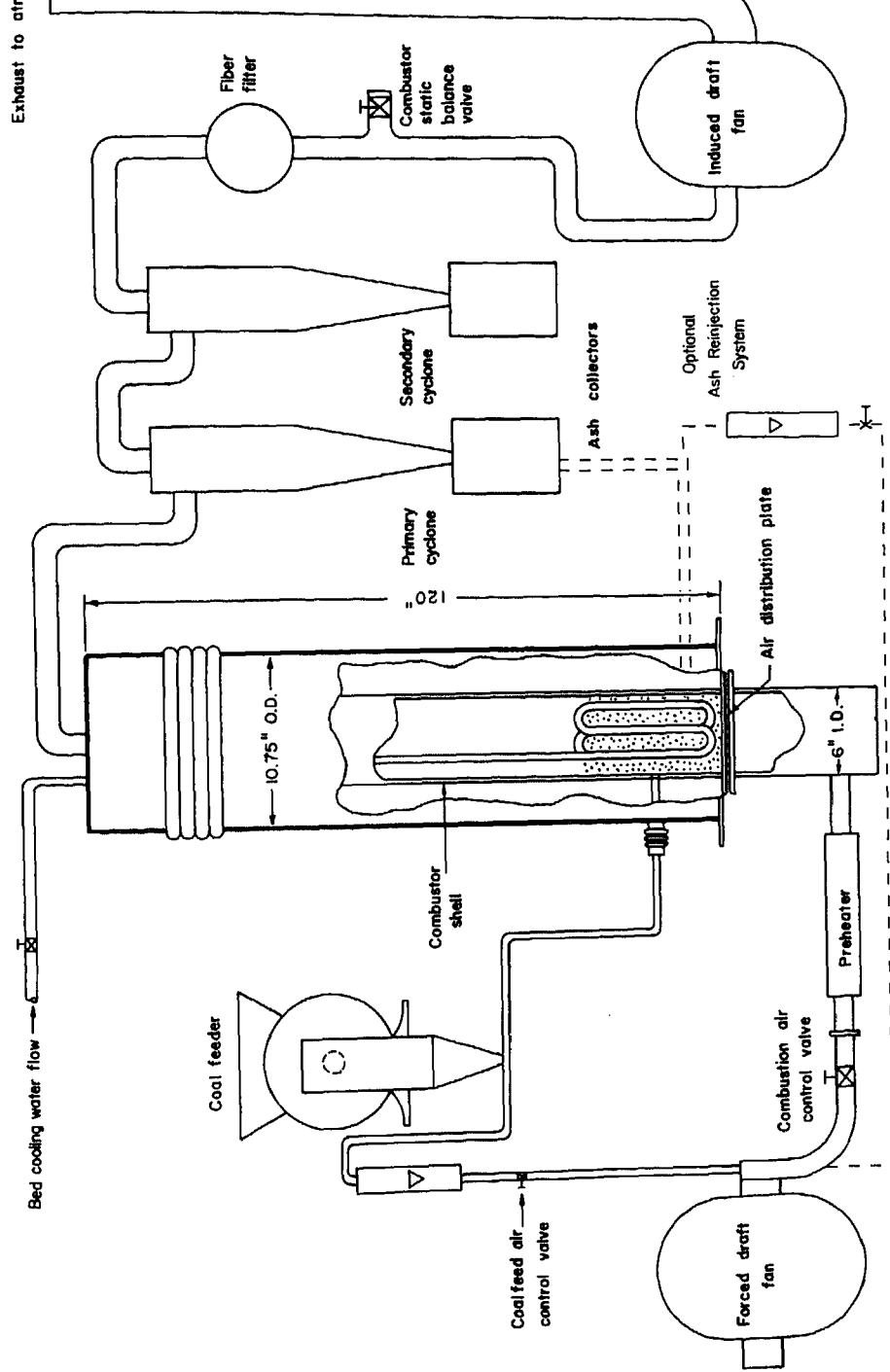
Figure 1. – Schematic of 6-inch diameter FBC at the Grand Forks Energy Technology Cent[er]

(Al2O3), and is added to the bed as a static or settled bed depth which becomes an expanded or fluidized-bed height of approximately 18 inches. The alundum bed is fluidized by air from the electric air preheater and combustion gases from a natural gas burner in the air plenum of the combustor. When a bed temperature of approximately 1000° F is reached, a small amount of coal is fed to the bed through the pneumatic injector. Using this technique, the bed is slowly brought up to operating temperature without an accumulation of coal in the bed. When the bed temperature reaches about 1300° F, the coal feeder is turned on continuously and a steady state condition is achieved.

The air flow to the bed is adjusted to obtain the superficial gas velocity at the desired temperature, which is controlled by regulating the water flow to the heat exchange tubes in the fluid bed. The desired air-fuel ratio is achieved by adjusting the speed of the coal screw feeder to obtain the required flue gas composition. When steady state conditions are achieved, data are taken over the desired operating time at one-hour intervals.

3. SAMPLE ANALYSIS

Coal for the combustion tests was prepared by crushing to a minus 1/8-inch mesh size. Prior to a combustion test, samples were obtained by riffling which were later analyzed for ultimate, proximate, sulfur forms, heating value, ash fusion temperature, and ash chemical analysis using X-ray fluorescence techniques. Samples of the coal fed to the combustor during a run are collected and made into a composite sample for determination of moisture, sulfur, ash, and chemical ash composition analysis for each run.

Fly ash collected during the dust loading procedures are analyzed by the X-ray fluorescence method for ten elements. In some cases, a sample of the ash was separated into particle size fractions by use of a Bahco size analyzer, and each fraction analyzed for the ten elements. The objective of analyzing each size fraction was to determine the distribution of the ten elements as a function of fly ash particle size. Several samples of the fly ash obtained from the combustion of Western coals in the fluidized bed have been examined using the scanning electron microscope (SEM). The objective was to determine if the fly ash particles are blinded by ash fusion.

The bed material samples obtained from the 6-inch AFBC are also analyzed on a routine basis for the ten elements using X-ray fluorescence techniques, and on an indefinite schedule using the SEM. Some agglomeration of the bed material at high temperatures was found to occur while using a high-sodium North Dakota lignite. The SEM has been used to analyze the surface of these agglomerations to determine the mechanism(s) of formation.

	Beulah Lignite	Wyodak Subbituminous
Coal ash, pct........................	7.49	5.91
Alkali-to-sulfur mole ratio.........	1.55	2.76
Ash analysis, pct:		
Silica, SiO_2........................	16.84	33.76
Aluminum oxide, Al_2O_3.............	11.16	16.43
Ferric oxide, Fe_2O_3...............	12.53	5.44
Titanium dioxide, TiO_2.............	1.68	0.89
Phosphorous Pentoxide, P_2O_5.......	0.63	1.28
Calcium oxide, CaO.................	23.26	22.07
Magnesium oxide, MgO...............	6.32	5.84
Sodium oxide, Na_2O................	4.95	1.68
Potassium oxide, K_2O..............	0.32	0.39
Sulfur trioxide, SO_3..............	22.32	12.17

Another possible explanation is the different superficial gas velocities at which the tests were run. The Wyodak coal demonstrated a 43 percent sulfur retention by the inherent coal ash alkali at 9 ft/sec superficial gas velocity and 1550° F average bed temperature. This data point is shown by the triangle in figure 3 and demonstrates a substantial increase in sulfur retention with decreased superficial gas velocity. Neglecting any effects of excess air differences, which have been shown to be minimal, the sulfur retention by the two coals would not be very different if the higher alkali-to-sulfur mole ratio for the Wyodak coal is considered. If Wyodak coal follows the general sulfur retention curve established at GFETC (shown in fig. 4) for the ten coals tested at 7 ft/sec and 1400° F, the sulfur retention should be about 80 percent. Tests on the ten Western coals have shown very little difference in sulfur retention with changes in superficial gas velocity in the range of 7 to 9 ft/sec (4). The effects of lower temperatures, shown in figure 3 for the Wyodak coal, combined with a change in superficial gas velocity, could easily bring the sulfur retention for the Wyodak coal in agreement with the data obtained for the other ten coals.

Nine Western coals in addition to the Beulah lignite and Wyodak subbituminous have been tested. The coal and ash analyses are shown in Table 1. Figure 4 shows the percent of coal sulfur retained by the coal ash alkali, denoted by the solid line, as a function of the inherent coal alkali-to-sulfur ratio for ten Western coals, including the Beulah lignite. The data presented for these ten coals are in good agreement with data obtained during the combustion of high-sulfur Eastern bituminous coal with limestone sorbent injection (5). Figure 4 also shows the data obtained using the Wyodak subbituminous coal with limestone addition at superficial velocities of 12 and 9 ft/sec. The dotted line shows the performance of the Wyodak coal at 12 ft/sec, and the dashed line at 9 ft/sec. The data points shown for the Wyodak coal at an alkali-to-sulfur mole ratio of 2.76 are for the inherent alkali only.

Table 1 shows some of the important coal and coal ash properties of the 11 different Western coals tested in the 6-inch AFBC at GFETC. The coals range in heating value from 13,098 Btu/lb moisture-free for the Utah bituminous coal, to 10,194 Btu/lb for the Velva, North Dakota lignite. The alkali-to-sulfur ratios for the 11 coals varies from 0.96 for the Utah coal to 5.96 for the Velva lignite.

Sulfur Retention

Figure 2 shows the sulfur retention by the coal ash alkali as a function of the average bed temperature while burning the Beulah, North Dakota lignite, which has an inherent calcium-to-sulfur mole ratio of 0.98. The sulfur retention without fly ash reinjection, denoted by the solid line, increased from 43 pct at an average bed temperature of 1250° F, to a maximum of about 53 pct at about 1440° F. At temperatures greater than 1440° F, the sulfur retention decreases. By reinjecting fly ash directly to the fluidized bed, an increase in both the optimum average bed temperature and sulfur retention was observed, as shown by the dashed line. Specifically, the maximum sulfur retention was increased to about 60 pct at an average bed temperature of 1500° F. In general, the sulfur retention obtained during ash reinjection tests is greater over the entire range of average bed temperatures tested, than the retentions obtained without fly ash reinjection.

Figure 3 shows the sulfur retentions by the coal ash as a function of average bed temperature while burning the Wyoming subbituminous coal from the Wyodak Anderson Canyon seam. The inherent calcium-to-sulfur (Ca/S) mole ratio was determined to be 1.92. The sulfur retention without fly ash reinjection, denoted by the solid line, generally decreased with increasing bed temperature, ranging from a maximum of 42 pct at 1350° F, to about 15 pct at 1500° F. The data obtained while reinjecting fly ash, denoted by the dashed line, shows only a small increase in the sulfur retention, and also decreases with increasing bed temperature. A direct comparison of sulfur retention data while burning the Beulah lignite and the Wyodak subbituminous coal cannot be made since the excess air and superficial velocities are not the same; it could, therefore, be expected that the sulfur retention profiles would be different.

There are several possible explanations for the difference in sulfur retention performance of the ash of the two coals tested. A very significant difference, shown in Table 2, is that the percent of sodium in the Beulah lignite is almost four times that in the Wyodak subbituminous coal. The silica in the Beulah lignite is about 60 percent of the concentration in the Wyodak coal. These differences in composition could be responsible for the different effects of temperature on the sulfur retention by the coal ash alkali.

TABLE 1. - Selected coal and ash properties

| Coal and Type	Coal Analysis Percent					Coal Ash Analysis Percent of Coal Ash					Stoichiometric Ratios	
	Moisture	Moisture-Free Basis				CaO	MgO	Na_2O	SiO_2	Al_2O_5	Calcium/ sulfur	Alkali/ sulfur
		Ash	Carbon	Sulfur	Heating value, Btu/lb							
Beulah North Dakota Lignite	27.13	10.28	64.77	1.38	10,820	23.3	6.3	5.0	16.8	11.2	0.98	1.55
Glenharold North Dakota Lignite	33.28	14.82	60.90	0.94	10,199	13.5	3.4	6.7	42.7	14.4	1.21	2.20
Baukol-Noonan North Dakota Lignite	30.73	9.94	64.45	0.56	10,706	16.5	3.7	9.9	30.7	18.3	1.66	3.10
Velva North Dakota Lignite	31.41	9.39	62.63	0.38	10,194	28.9	8.1	2.2	22.6	12.4	4.09	5.96
Decker Montana Subbituminous	20.50	5.25	70.63	0.41	12,056	16.0	3.8	7.7	30.6	17.8	1.19	2.10
Colstrip Montana Subbituminous	24.01	10.19	65.39	0.87	10,996	14.7	4.3	0.1	32.7	19.1	0.98	1.39
Sarpy Creek Montana Subbituminous	23.72	11.80	66.74	0.90	11,272	18.3	2.8	3.6	34.1	18.4	1.36	1.90
Naughton Wyoming Subbituminous	20.42	6.29	68.37	0.47	11,921	7.3	3.0	0.6	57.8	16.2	0.56	0.93
Big Horn Wyoming Subbituminous	21.35	5.60	68.71	0.45	11,595	16.3	5.7	4.6	28.4	16.2	1.14	1.98
Browning Utah Bituminous	3.59	7.89	74.27	0.97	13,098	13.4	3.3	2.7	40.6	17.0	0.63	0.96
Wyodak Wyoming Subbituminous	29.50	8.38	68.71	0.55	11,563	22.1	5.8	1.7	33.8	16.4	1.92	2.76
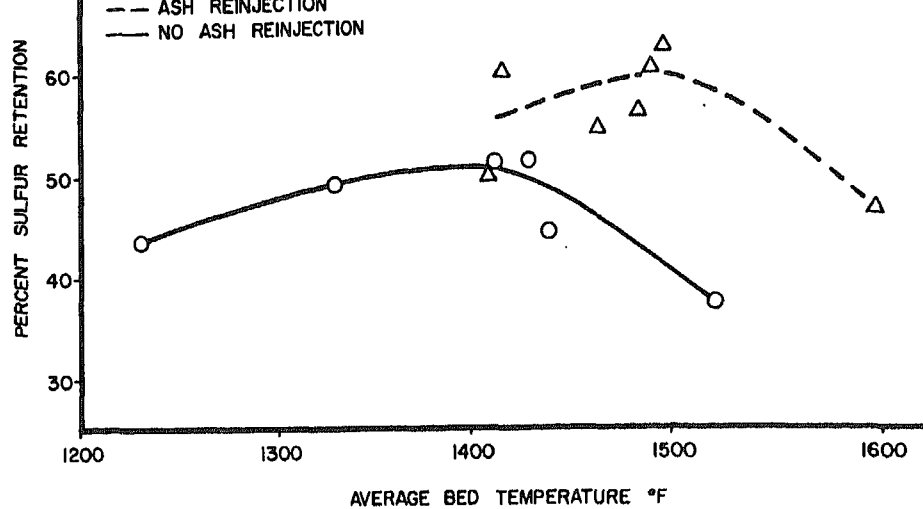
Figure 2. - Sulfur retention as a function of average bed
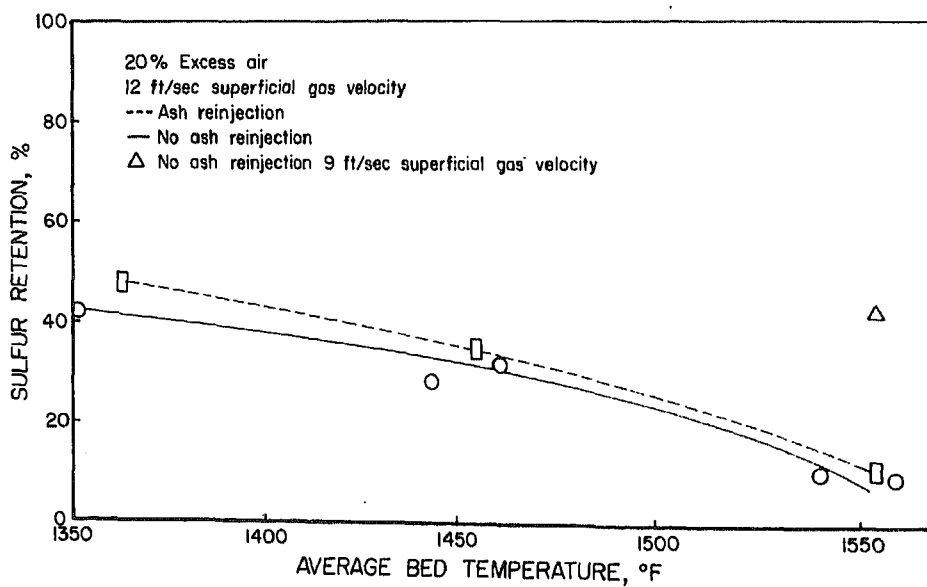temperature using Beulah, N. Dak. lignite.

Figure 3. - Sulfur retention as a function of average bed
temperature using Wyoming subbituminous coal
from the Wyodak Anderson Canyon seam.

	Beulah Lignite	Wyodak Subbituminous
Coal ash............................	7.49	5.91
Inherent alkali-to-sulfur mole ratio........................	1.55	2.76
Silica, SiO_2...........................	16.84	33.76
Aluminun oxide, Al_2O_3...............	11.16	16.43
Ferric oxide, Fe_2O_3.................	12.53	5.44
Titanium dioxide, TiO_2..............	.1.68	0.89
Phosphorous 1 Pentoxide, P_2O_5.......	0.63	1.28
Calcium oxide, CaO..................	23.26	22.07
Magnesium oxide, MgO................	6.32	5.84
Sodium oxide, Na_2O.................	4.95	1.68
Potassium oxide, K_2O...............	0.32	0.39
Sulfur trioxide, SO_3...............	22.32	12.17

Another possible explanation is the different superficial gas velocities at which the tests were run. The Wyodak coal demonstrated a 43 percent sulfur retention by the inherent coal ash alkali at 9 ft/sec superficial gas velocity and 1550° F average bed temperature. This data point is shown by the triangle in figure 3 and demonstrates a substantial increase in sulfur retention with decreased superficial gas velocity. Neglecting any effects of excess air differences, which have been shown to be minimal, the sulfur retention by the two coals would not be very different if the higher alkali-to-sulfur mole ratio for the Wyodak coal is considered. If Wyodak coal follows the general sulfur retention curve established at GFETC (shown in fig. 4) for the ten coals tested at 7 ft/sec and 1400° F, the sulfur retention should be about 80 percent. Tests on the ten Western coals have shown very little difference in sulfur retention with changes in superficial gas velocity in the range from 7 to 9 ft/sec (4). The effects of lower temperatures, shown in figure 3 for the Wyodak coal, combined with a change in superficial gas velocity, could easily bring the sulfur retention for the Wyodak coal in agreement with the data obtained for the other ten coals.

Nine Western coals in addition to the Beulah lignite and Wyodak subbituminous have been tested. The coal and ash analyses are shown in Table 1. Figure 4 shows the percent of coal sulfur retained by the coal ash alkali, denoted by the solid line, as a function of the inherent coal alkali-to-sulfur ratio for ten Western coals, including the Beulah lignite. The data presented for these ten coals are in good agreement with data obtained during the combustion of high-sulfur Eastern bituminous coal with limestone sorbent injection (5). Figure 4 also shows the data obtained using the Wyodak subbituminous coal with limestone addition at superficial velocities of 12 and 9 ft/sec. The dotted line shows the performance of the Wyodak coal at 12 ft/sec, and the dashed line at 9 ft/sec. The data points shown for the Wyodak coal at an alkali-to-sulfur mole ratio of 2.76 are for the inherent alkali only.
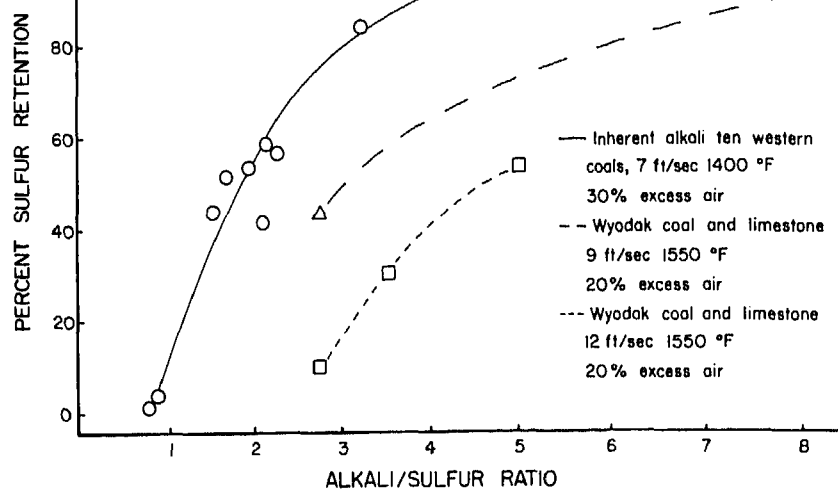
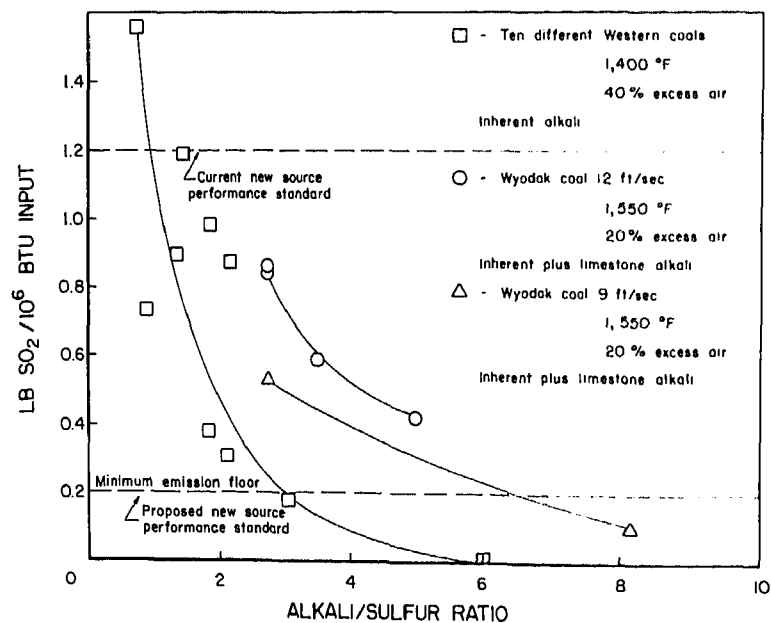Figure 4. - Sulfur retention versus total
alkali-to-sulfur ratio.

Figure 5. - Sulfur dioxide emission level as a
function of alkali-to-sulfur ratio.

strate that all but one of the coals tested meet the current New Source Performance Standard of 1.2 lb $SO_2/10^6$ Btu, without the addition of sorbent material. The Beulah lignite was marginal, and in some tests at slightly different operating conditions, the emission level exceeded this standard. The 85 percent removal standard point is not shown on figure 5 because the coal sulfur varied from 0.26 percent for the Velva lignite to over 1.0 percent for the Beulah lignite. The two coals which show emission levels below the proposed 0.2 lb $SO_2/10^6$ Btu minimum emission floor are the Velva lignite and the Baukol-Noonan lignite. The Wyodak coal meets the current standard at all conditions tested, and would meet the proposed standard at an alkali-to-sulfur mole ratio of approximately 6.5. This would require a limestone feed rate of about 0.05 lb per lb of coal with the Linwood limestone used for these tests (6).

Nitrogen Oxide Emissions

The nitric oxide (NO) emissions were also measured during the tests of the various Western coals, as well as over the range of operating conditions studies performed while burning the Beulah, North Dakota lignite. The largest effects on the emission of NO are due to variation in average bed temperature, and percent of excess air. The change in nitric oxide emissions with superficial gas velocity was examined while burning the Beulah, North Dakota, lignite, and no change over a range of 5 to 12 ft/sec was observed (4). The same observation was made while burning the other Western coals at two different fluidizing velocities. Figure 6 shows the nitric oxide emission level as a function of the average bed temperature for the Beulah, North Dakota, lignite, and the Wyodak, Wyoming, subbituminous coal. The Wyodak tests were performed at 12 ft/sec superficial gas velocity and 20 percent excess air, and the tests using Beulah lignite were at 7 ft/sec and 30 percent excess air. All data, except one point for the Beulah lignite at the highest bed temperature, are below the current NO_x emission standard of 0.7 lb $NO_x/10^6$ Btu for bituminous coal. The proposed new standard of NO_x emissions for subbituminous coal is 0.5 lb $NO_x/10^6$ Btu. The Wyodak coal at all test conditions emitted NO_x at levels below this standard; however, the Beulah coal did not meet the proposed standard at temperatures above 1350° F and 30 percent excess air. Figure 7 shows the nitric oxide emission data obtained with five of the 11 Western coals tested as a function of excess air at 1400° F average bed temperature. This curve illustrates the large dependence of nitric oxide emissions on excess air; as would be expected, the more oxygen available for reaction, the more nitric oxide formed. This curve shows that at excess air levels below approximately 40 percent, all of the coals for which data are shown can meet the current bituminous coal standard; however, only at excess air levels below approximately 15 percent will these coals meet the proposed standard of 0.5 lb $NO_x/10^6$ Btu.
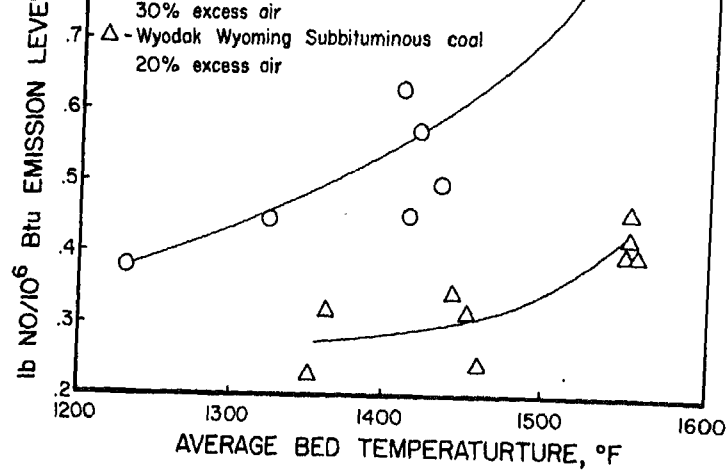
30% excess air
△-Wyodak Wyoming Subbituminous coal
20% excess air

Figure 6. - Nitric oxide emission level as a function
of average bed temperature.

O-Kemmerer Wyoming Subbituminous
△-Beulah North Dakota Lignite
□-Browning Utah Bituminous
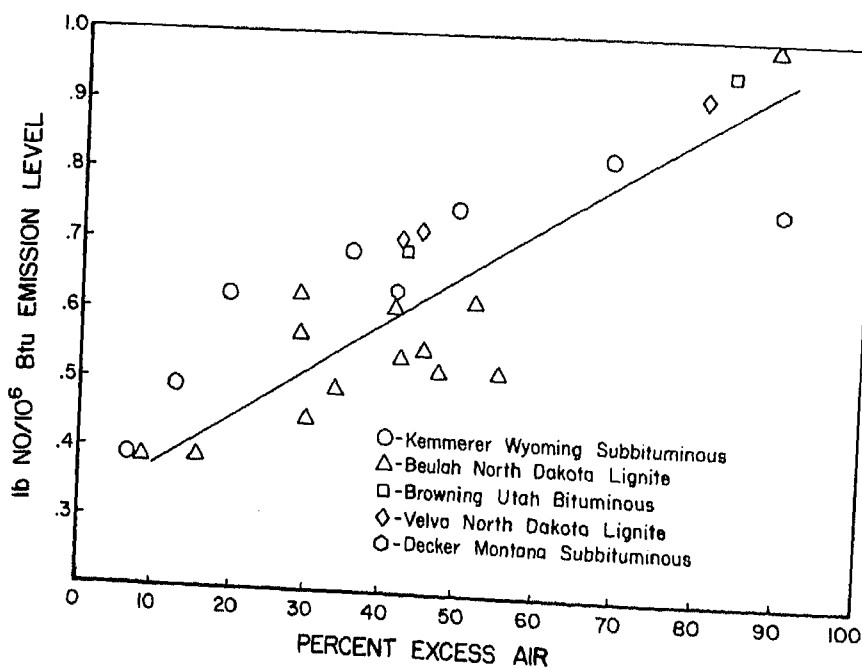◇-Velva North Dakota Lignite
O-Decker Montana Subbituminous

Figure 7. - Nitric oxide emission level as a function
of excess air.

a test condition of 1500° F for approximately 12.5 hours, fused pieces of bed material appeared in the removed bed material. Some of these agglomerations appear to have been formed on cooling tubes or thermocouple wells. This agglomerated bed material later broke off and fell to the bottom of the bed. Figure 8 shows the largest of the agglomerations. This formation is approximately 1-1/2 inches long, 1/4 inch wide, and 3/8 inch deep, and appears to have been formed on a cooled tube. Figure 9 is a 60X magnification of a single particle (1 x 1/2 mm) from what appears to be the tube side, or unfused side, of the agglomeration. In figure 10 this same particle is magnified 900 times, showing what appears to be partial melts on the surface. An analysis of the partially melted material next to the tube surface was made using the scanning electron microscope. An analysis, presented in Table 3, shows a substantial enrichment of sodium as compared to the coal ash analysis (approximately 6 percent sodium oxide). Figure 11 shows the outer, entirely fused surface at 900X magnification, and illustrates that this surface is quite different and essentially void of the partial melts that appeared on the surface of the tube-side material. An analysis of a random location on the surface of the outer fused area is shown in Table 4. This outer surface has only a slight enrichment in sodium, which would suggest that the deposits formed on the tube are associated with the condensation of sodium and sulfur as sodium sulfate. The sodium material is volatilized out of the material as it grows away from the cooled surface and is fused. Since calcium is not lost, the ratio of total alkalinity to sulfur is greater in the fused surface (ratio = 2.1) than in the tube-side materials (ratio = 1.0).

TABLE 3. - <u>Surface analysis of single particles from tube side of agglomeration</u>

Na_2O	24.3
MgO	2.8
Al_2O_3	3.4
SiO_2	3.2
P_2O_5	0.3
SO_3	48.7
K_2O	4.7
CaO	9.3
Fe_2O_3	3.3
TiO_2	0.0
TOTAL	100.0

TABLE 4. - <u>Surface analysis of fused side of agglomeration</u>

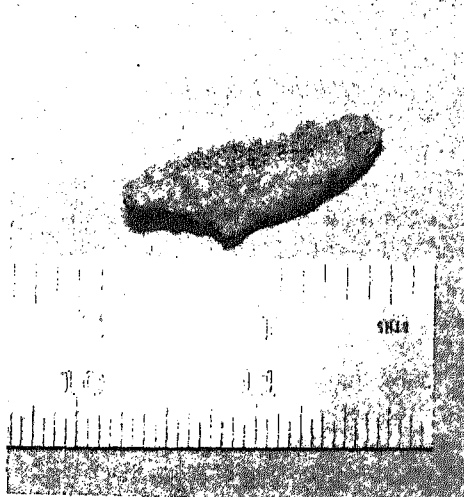|	
Na_2O	8.7
MgO	4.8
Al_2O_3	6.7
SiO_2	8.7
P_2O_5	0.2
SO_3	30.1
K_2O	0.4
CaO	30.1
Fe_2O_3	9.3
TiO_2	1.0
TOTAL	100.0

Figure 8. - Agglomeration
formed in bed with high-
sodium lignite.

Figure 9. - Single particle
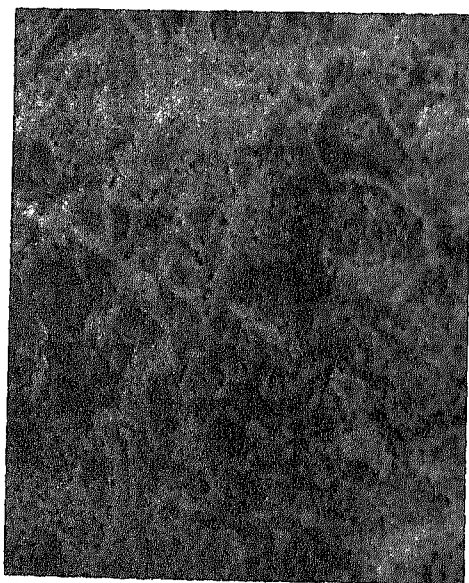from agglomeration shown
at 60X magnification.

Figure 10. - Single particle
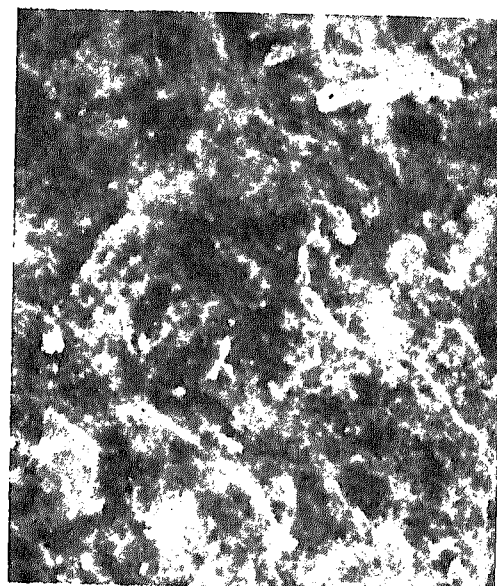from agglomeration shown
at 900X magnification.

Figure 11. - Fused surface
of agglomeration shown at
900X magnification.

loading sample using the ASME sampling method with a large filter and housing was performed to obtain a particulate sample for physical and chemical characterization. Figure 12 shows the particle size distribution obtained from sieve analysis for particles larger than about 40 microns, and by Bahco analysis for less than 30 microns. Fifty percent of the sample on a weight basis was less than about 60 microns, with about 10 percent less than 10 microns. Several of the size fractions were analyzed for ten different elements by use of X-ray fluorescence analysis. Table 5 shows the analysis of selected size fractions as a percent of the sample fraction, and percent of the total sample. The analyses indicate a general enrichment of calcium and sulfur in the small size fractions, and a depletion of iron in the small particle sizes. A float-sink analysis of the Beulah lignite shows that iron is enriched in the sink fraction and that calcium and sodium are depleted. Therefore, it is believed that the iron is largely associated with the extrinsic coal ash, and the calcium and sodium are associated with the intrinsic ash, or organically bound mineral matter. This would lead to the enrichment of the calcium sulfate in the small size fractions, as shown in Table 5.

Tests were performed in a similar way while burning the Beulah lignite with sodium chloride injection. No improvement in sulfur capture was noted during these tests, but it was found that the size distribution of the fly ash was substantially enlarged. Figure 12 shows the size distribution of the dust loading sample obtained during this run. Fifty percent of the sample by weight was less than 100 microns, and 95 percent of the sample was greater than 40 microns; without salt injection, only 60 percent of the sample was greater than 40 microns.

Tests showing the particulate size fractions and the chemical analysis of the fractions collected in the primary cyclone following the AFBC have been previously presented (7). The collected ash accounted for 86 percent of the fly ash emitted from the FBC. The data showed that 50 percent of the collected particles were less than 60 microns. The chemical compositions of seven size fractions of the particulate, shown in Table 6, were determined by X-ray fluorescence analyses. The data indicate that the silica and alumina were relatively enriched in the collected fly ash, as compared with the concentrations in the muffle furnace ash, and that sodium, calcium, and iron oxides are relatively depleted.
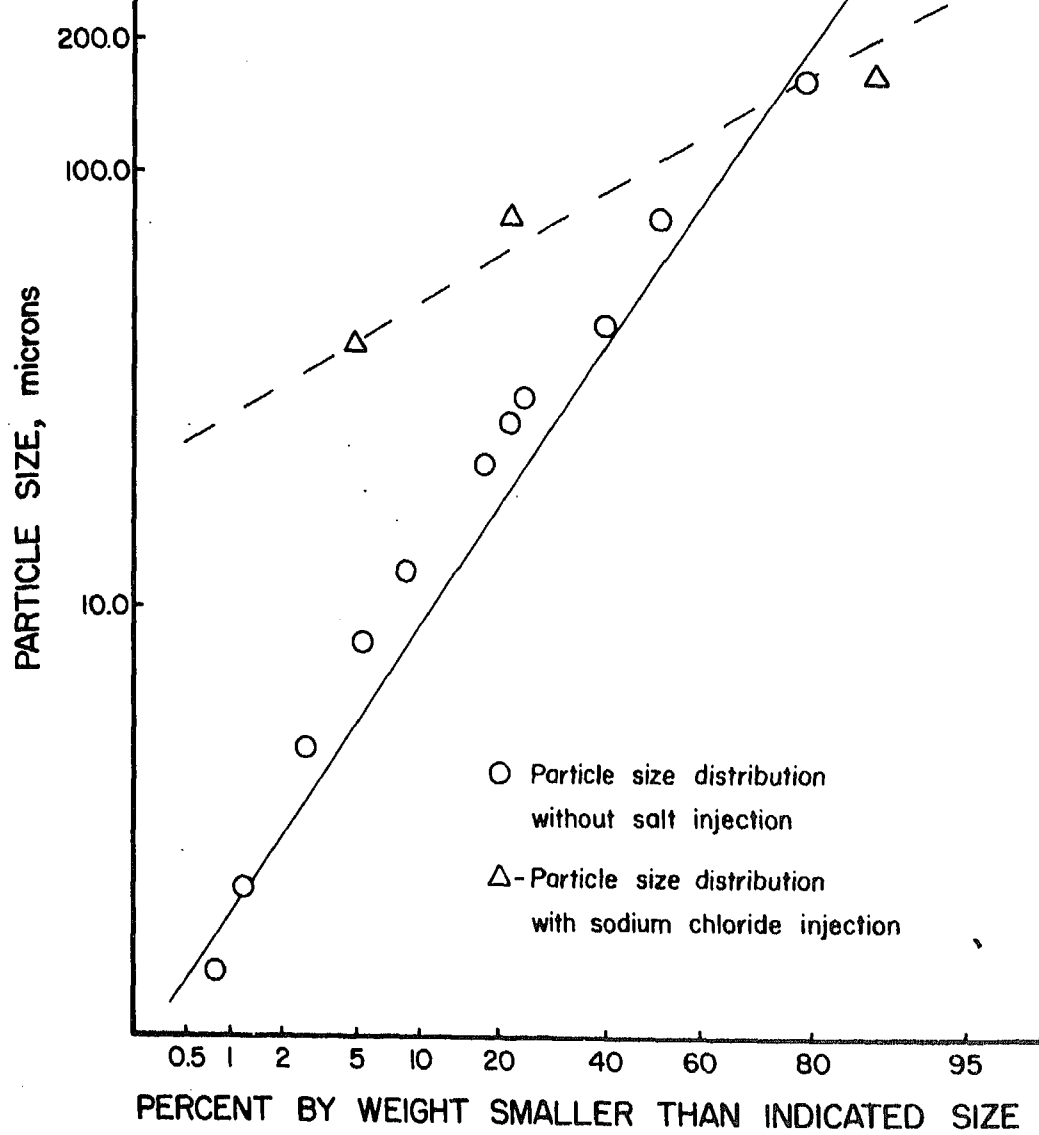
Figure 12. - Dust loading sample particle size distribution.

TABLE 5. – Analysis of size fractions from dust loading sample

	300-150 microns		150-75 microns		75-44 microns		29.5-26 microns		12-8.2 microns		4.7-2.25 microns		2.25 micron	
	Pct fraction	Pct total	Pct fraction	Pct total	Pct fraction	Pct total	Pct fraction	Pct total	Pct fraction	Pct total	Pct fraction	Pct total	Pct fraction	Pct total
Loss on ignition............	25.9	3.68	4.4	1.18	0.2	0.03	1.0	0.15	10.4	0.37	12.4	0.20	10.7	
Silica, SiO2...............	14.3	2.03	25.4	6.80	26.9	2.97	32.4	4.88	17.5	0.61	13.9	0.22	12.4	
Aluminum oxide, Al2O3........	10.5	1.49	13.8	3.70	12.5	1.39	12.9	1.95	12.6	0.44	12.6	0.20	13.2	
Ferric oxide, Fe2O3.........	29.3	4.16	20.3	5.45	16.8	1.89	9.5	1.43	5.8	0.20	5.2	0.08	4.7	
Titanium dioxide, TiO2......	0.2	0.03	0.4	0.11	0.5	0.06	0.5	0.08	0.5	0.02	0.5	0.01	0.4	
Phosphorous pentoxide, P2O5.............	0.2	0.03	0.5	0.13	0.6	0.07	0.6	0.09	0.7	0.02	0.7	0.01	0.8	
Calcium oxide, CaO..........	9.0	1.28	20.1	5.39	26.3	2.90	24.7	3.72	27.9	0.98	27.7	0.44	28.2	
Magnesium oxide, MgO........	2.4	0.34	5.5	1.48	6.8	0.75	6.8	1.03	7.9	0.28	8.1	0.13	9.0	
Sodium oxide, Na2O..........	2.1	0.30	4.0	1.08	3.3	0.37	3.8	0.58	4.1	0.15	4.0	0.06	4.8	
Potassium oxide, K2O........	0.2	0.03	0.1	0.03	0.2	0.02	0.2	0.03	0.2	0.01	0.2	*	0.2	
Sulfur trioxide, SO3........	5.7	0.81	5.4	1.45	5.7	0.64	7.4	1.12	12.4	0.43	14.7	0.24	15.5	

* Percent of total sample less than 0.01 percent.

Particle Size Microns	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	SO_3
Plus 149 sieve analysis	22.1	21.5	8.6	1.3	0.8	23.3	7.8	3.0	0.4	11.2
149 - 74 sieve analysis	38.1	30.4	7.9	1.3	0.3	9.6	3.5	2.5	0.7	5.7
74 - 44 sieve analysis	50.4	13.3	8.5	0.9	0.4	12.1	5.1	3.8	0.3	5.1
44 - 21 aerodynamic size Bahco	36.8	18.2	8.6	0.9	0.9	19.3	7.1	3.0	0.1	5.1
21 - 8.2 aerodynamic size Bahco	30.6	21.9	8.0	0.9	0.9	20.7	6.3	3.3	0.2	7.1
8.2 - 2.3 aerodynamic size Bahco	33.0	21.1	8.1	1.0	1.0	19.7	7.8	1.3	0.2	6.7
Minus 2.3 aerodynamic size Bahco	26.3	20.7	8.0	1.1	0.7	22.3	7.3	3.8	0.3	9.6
Bulk sample analysis	38.0	19.9	9.0	1.1	0.4	16.7	5.3	2.8	0.3	6.6
Muffle furnace coal ash	16.8	11.2	12.5	1.7	0.6	23.3	6.3	4.9	0.3	22.3

5. CONCLUSIONS

There are four general conclusions that can be made from these data.

1.   Most Western coals, when burned in an atmospheric fluidized-bed combustor, can meet or better the current New Source Performance Standard of 1.2 lbs $SO_2/10^6$ Btu. Most of these coals, however, will not meet the proposed NSPS without the additional use of sulfur sorbent.

2.   The emissions of nitric oxide from the fluidized combustion of Western coals are, as expected, very dependent on the average bed temperature and the percent of excess air. Most of the coals tested will meet the current NSPS of 0.7 lbs $NO_x/10^6$ Btu for bituminous coal, but will not meet the proposed standard

possible thermal efficiency, and the data then indicate a NO_x level below the standard is possible.

3. The fluidized-bed combustion of high-sodium Western coals may exhibit a problem of bed agglomeration because of the coating of bed particulate with the sticky sodium sulfate material.

4. The particulate generated in an AFBC with the addition of sodium chloride is much coarser than that which is generated without salt injection. This may be a useful procedure for the agglomeration of particulate to aid in collection.

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7. Goblirsch, Gerald M., et al. Effects of Coal Composition and Ash Reinjection on Sulfur Retention Burning Lignite and Western Subbituminous Coals. Fifth International Conference on Fluidized-Bed Combustion, Washington, D.C., December 12-14, 1977.

Presented by

Joseph Epstein
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MHD Division

I INTRODUCTION

The control of nitrogen oxide (NOx) emissions from coal-fired power plants, including Magnetohydrodynamic (MHD) systems, is a concern which most often appears in the evaluation of a new technology. Since the 1960's, the MHD community has given considerable attention to NOx control and has directed significant effort in research, analysis and experimental activities focused on reducing NOx emissions to presently proposed standards and to values which may become the standards in the period of commercialization.[1,2]

Present information indicates that both current and future NOx standards can be met by the MHD process, even though no credit is provided for the significant increase in net plant efficiency over conventional power-plant systems.

Presently available results from experiments as high as 8 MWt and from calculations based on experimentally derived kinetics data have served to empirically identify realistic NOx control techniques. The preferred system operation is to: (a) operate the coal combustor fuel rich, (b) cool the gas slowly in a radiant boiler downstream of the MHD channel/diffuser (the radiant boiler is the key component in MHD NOx control), and (c) add additional air to the radiant-boiler exhaust, at a temperature high enough to complete combustion but low enough to minimize the tendency to form additional NOx. These concepts are discussed in detail along with experimental and analytical results that have been obtained to verify that the method of control is technically sound and practical. Current DOE-sponsored development efforts are aimed at optimizing the method and at formal demonstration in suitable facilities.[3]

II GENERAL TECHNICAL DISCUSSION

Open-Cycle Coal-Fired MHD

A typical open-cycle MHD topping cycle with a directly fired air preheater and a conventional steam turbine bottoming cycle is illustrated schematically in Fig. 1. Preheated, compressed air and coal fuel are burned in a fuel-rich environment under pressure and at very high temperatures ($2800^{\circ}K = 4580^{\circ}F$) in the combustor. Potassium seed is injected, and the combustion gas/seed mixture is fed into the MHD channel, which produces DC electrical power that is then converted to AC power. The combustion gases then pass through a diffuser where the remaining kinetic energy is recovered. The exhaust gases leaving the MHD generator are still at high temperature ($2200^{\circ}K = 3500^{\circ}F$). This residual heat
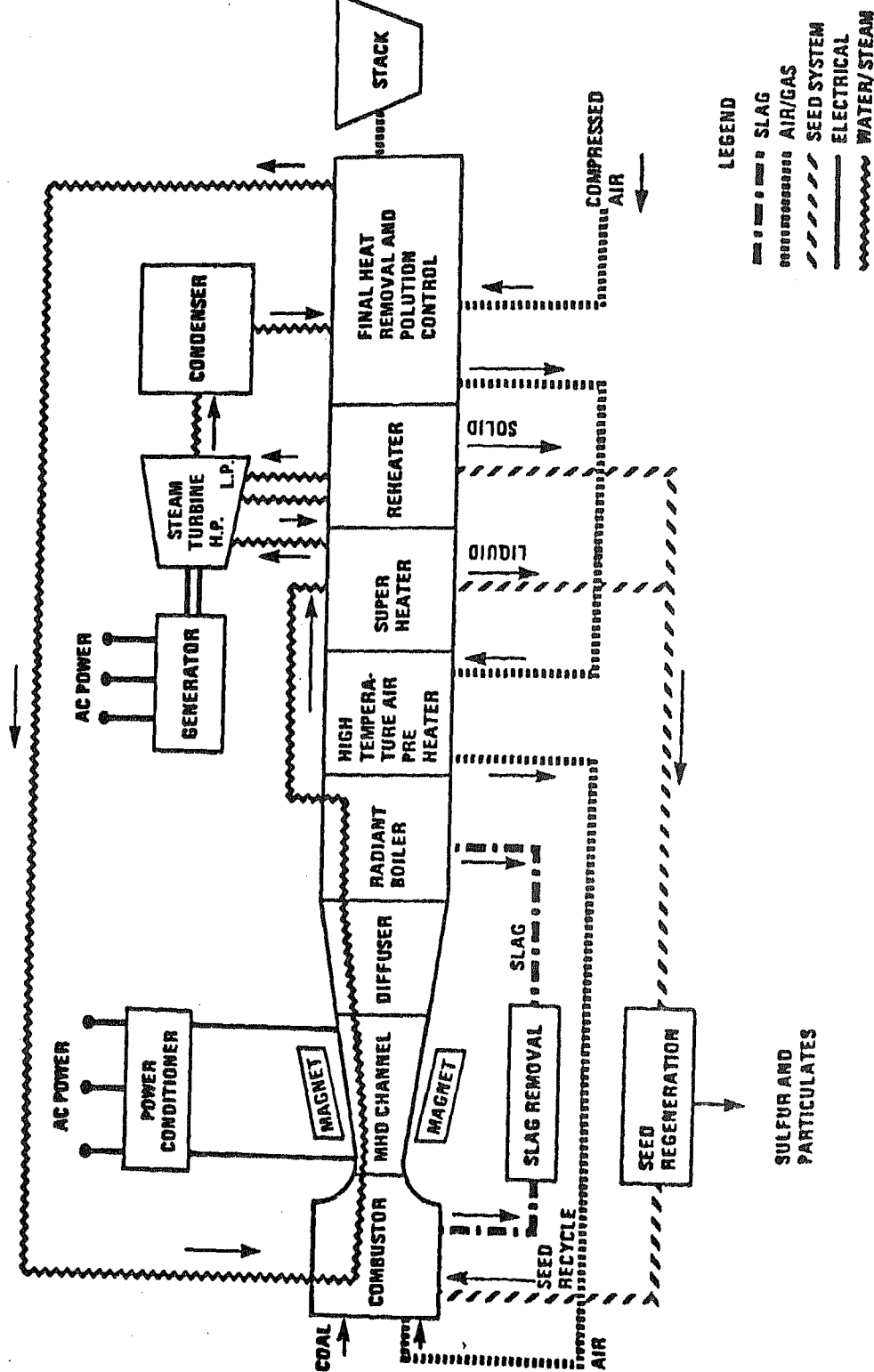
FIGURE 1. SCHEMATIC OF OPEN-CYCLE COAL-FIRED MHD SYSTEM.

additional air is added and combustion is completed. The combustion gas then flows to the air preheaters where heat is extracted and used to preheat the air which is fed to the combustor. Heat from the walls of the radiant boiler is used to heat steam, which then is super-heated and utilized in the steam turbines. Most of the spent seed is condensed from the gas as potassium sulfate. After leaving the air and steam heaters, most of the combustion gases flow through the economizers and to particulate control devices, where additional seed material is collected, before leaving the stack.

Combustor

Summarized in Table I are the principal differences between MHD and conventional coal combustion. In the MHD combustor, both the flame temperature and pressure are significantly higher, at approximately 2800°K and 6 to 10 atmospheres. While a higher temperature leads to higher initial NO concentrations, there are several distinct advantages that accrue from an overall greater system temperature in the MHD case. First, there is no downstream soot formation. Second, fuel-nitrogen is rapidly equilibrated with the other combustor gases, whereas in conventional coal combustion a large fraction of the fuel-nitrogen can be "frozen out" as NOx. These observations on soot and fuel-nitrogen for the MHD case have been confirmed by experiments at UTSI where coal was burned 15% fuel-rich with nearly pure oxygen resulting in <50 ppm NOx in the exhaust.[4-6]

MHD Channel/Diffuser

With preheated air as the oxidant, the equilibrium NO concentration in the MHD coal combustor is about 1% for equivalence ratios between 0.9 and 1.0, or approximately 10 times that of a conventional combustor. But, because of the relatively high gas temperature in the MHD channel/diffuser, the NO concentration at the diffuser exit is not far from its equilibrium value. Representative values are 1000 to 3000 ppm (molar) for a 5 to 10% fuel-rich mixture. This is illustrated in Fig. 2. Fuel-rich operation shows its importance in this region since the NO equilibrium value is a strong function of equivalence ratio at the gas temperatures typical of the channel/diffuser. It is the equilibrium value which acts as the "driving force" for the finite rate chemistry, with the approach rate limited by rate constants that are exponential functions of temperature. By defining t_{eff} as the reciprocal of the effective rate, this can be represented schematically as

$$- \frac{d[NO]}{dt} \sim \frac{[NO]-[NO]_{equilibrium}}{t_{eff}}$$

The balance between NO concentration and rate dependence becomes critical (~ 1 sec, $[NO] \sim [NO]_{NSPS}$) at temperatures below 2300°K; that is, in the radiant boiler. Therefore, what occurs in the radiant boiler controls the NOx emission for open-cycle MHD systems.

TABLE I
COMPARISON OF
MHD AND CONVENTIONAL COAL COMBUSTION

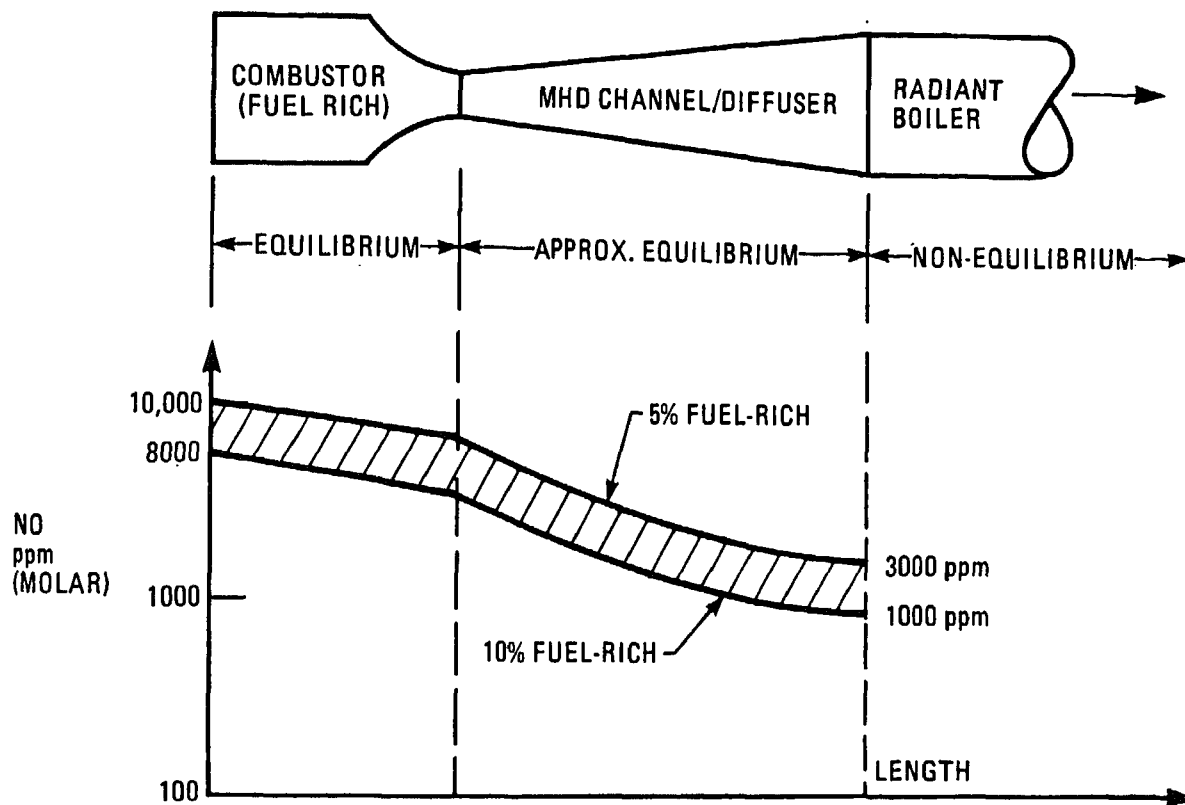|	COMBUSTOR FLAME TEMP.	COMBUSTOR PRESSURE	DOWNSTREAM SOOT	FUEL NITROGEN	NET-PLANT EFFICIENCY
MHD	~2800° K (4580°F)	6 - 10 atm.	None, due to higher system temperature	Equilibrated with air N_2	lb. NO_x per MWe less for MHD
CONVENTIONAL	~1800° K (2780°F)	1 - 2 atm.	Greater tendency than in MHD	Large fraction frozen as NO_x	- -

FIGURE 2.   REPRESENTATION OF NO$_x$ CONCENTRATION VERSUS LENGTH
            ALONG FLOW TRAIN.

subject of many detailed studies.[2],[7]-[12] The cooling rate (°K/sec) of the gas is the critical design parameter, which determines the NOx concentration in the effluent of the MHD system.[2],[7]-[12] Generally, the slower the cooling the lower the NOx. Since the rate constants are nonlinear functions of temperature, the optimum cooling rate is also nonlinear. Performance calculations for radiant boilers show that, as the name implies, the gas cools by radiating to the walls of the boiler. Detailed calculations, using experimentally-determined rate constants, have included the effects of spectral radiation, thermal boundary layers, buoyancy, and particulate radiation.[9]-[11] These calculations show that the NOx levels at the exit plane of the boiler can be kept below the New Source Performance Standards (NSPS), present and contemplated, by proper design of the unit.

As mentioned earlier, the radiant boiler is the critical component in controlling NOx emissions from an open-cycle MHD plant. It is discussed in greater detail in Section III.

High Temperature Air Preheater

Hot air for the coal combustor is provided by the high temperature air preheater (HTAH). The HTAH also provides the location for the injection of additional air to burn the remaining fuel in the fuel-rich gas stream. At the temperatures encountered in the HTAH, the gas is still hot enough so that soot does not form. Combustion is essentially that of a low Btu gas $(CO + H_2)$, and is rapid with a time scale on the order of tens of milliseconds.[7],[11]

New Source Performance Standards (NSPS)

Summarized in Table II are the present, and proposed NSPS for NOx emissions for the combustion of a sub-bituminous coal[14]. The standards are set in units of lb-NO_2 per million Btu-fired, but, in Table II, the approximate equivalent in mass and molar parts-per-million (ppm) is also given. The equivalent ppm is a function of stoichiometry, coal moisture content, coal type, and the chemical composition of the combustion gas.

III   RADIANT BOILER AND NOx CONTROL

Analysis and Experimental Data

Detailed computer calculations, based on experimentally derived kinetics data, have identified the gas-cooling rate (°K/sec) as the critical parameter in radiant boiler design for the purpose of controlling NOx stack emissions in MHD plants. The results of such computations may be presented in a number of ways, and these are exhibited in Figs. 3 to 6, inclusive.

One can depict the asymptotic behavior of NOx concentration as a function of radiant boiler length (or height) for different cooling rates. This is shown

TABLE II
NO$_x$ STANDARDS

STANDARD	LB. NO$_x$ PER MBtu FIRED	EQUIV. PPM (MASS)	EQUIV. PPM (MOLAR)
PRESENT	0.7	~825	~550
PROPOSED	0.5 (SUB-BITUM) 0.6 (BITUM)	~580 ~710	~390 ~475

RADIANT BOILER: FREEZING OF NO_x VERSUS COOLING RATE AND LENGTH (OR HEIGHT)

1000

NO ppm (MOLAR)

500

1000° K/SEC. = COOLING RATE

10% FUEL-RICH

500° K/SEC. = COOLING RATE

250° K/SEC. = COOLING RATE

0

LENGTH (OR RADIANT-BOILER HEIGHT)
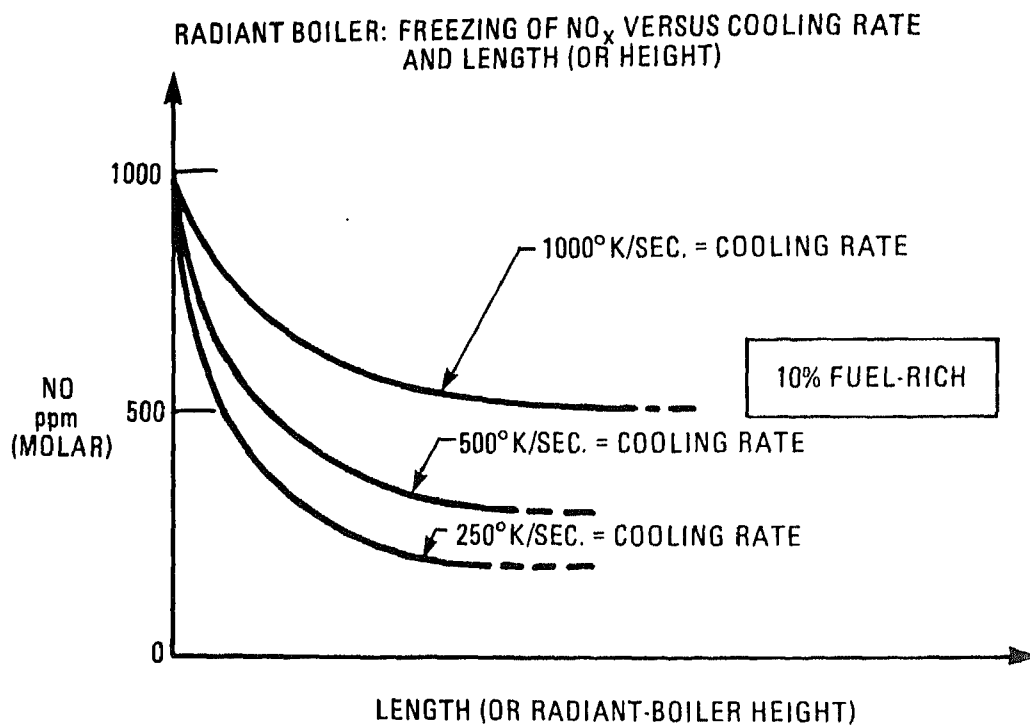
FIGURE 3. FREEZING OF NO_x VERSUS COOLING RATE AND LENGTH (OR HEIGHT) OF RADIANT BOILER.
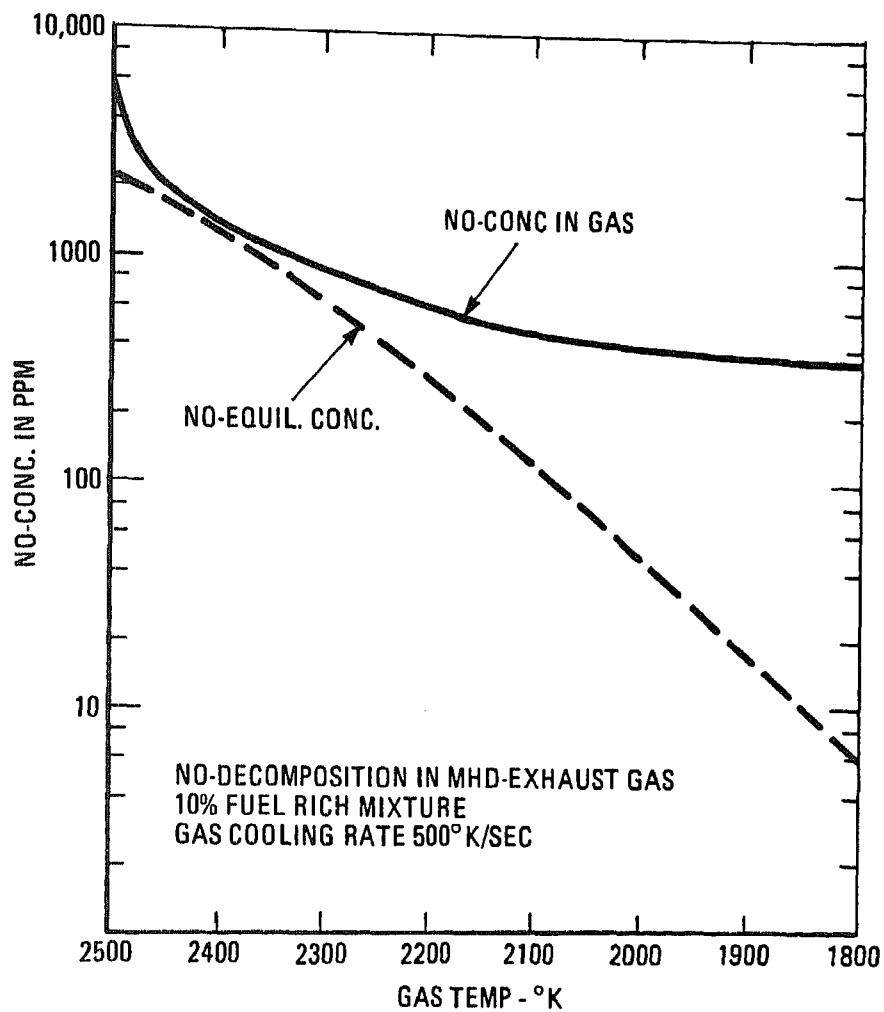
FIGURE 4. NO-DECOMPOSITION IN MHD-EXHAUST GAS FOR 10% FUEL RICH MIXTURE AND CONSTANT GAS COOLING RATE OF 500°K/SECOND (TAKEN FROM REF. 7)
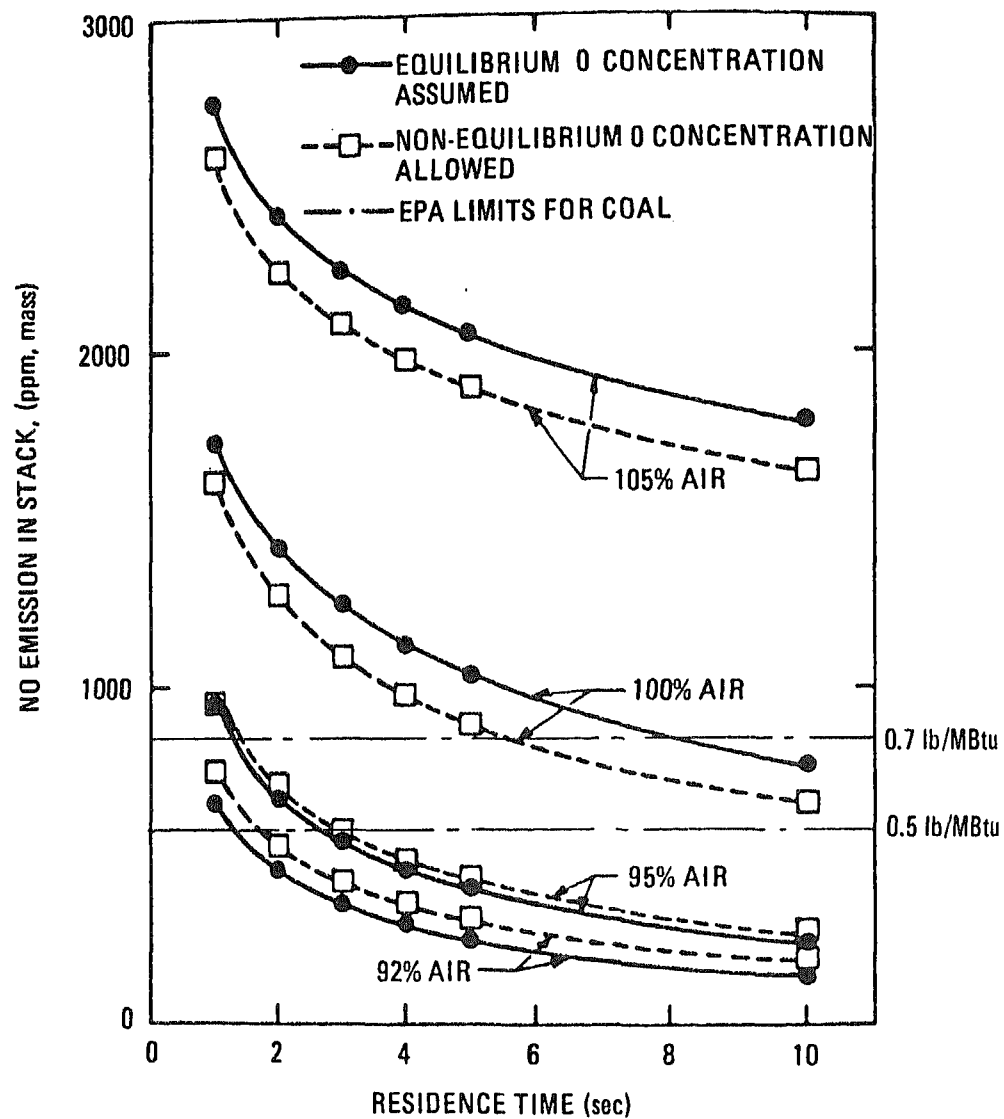
FIGURE 5. NO EMISSIONS IN AN MHD POWER PLANT AS A FUNCTION OF RESIDENCE TIME FOR THE RADIANT BOILER AND AIR PRE-HEATER   (TAKEN FROM REF. 2)
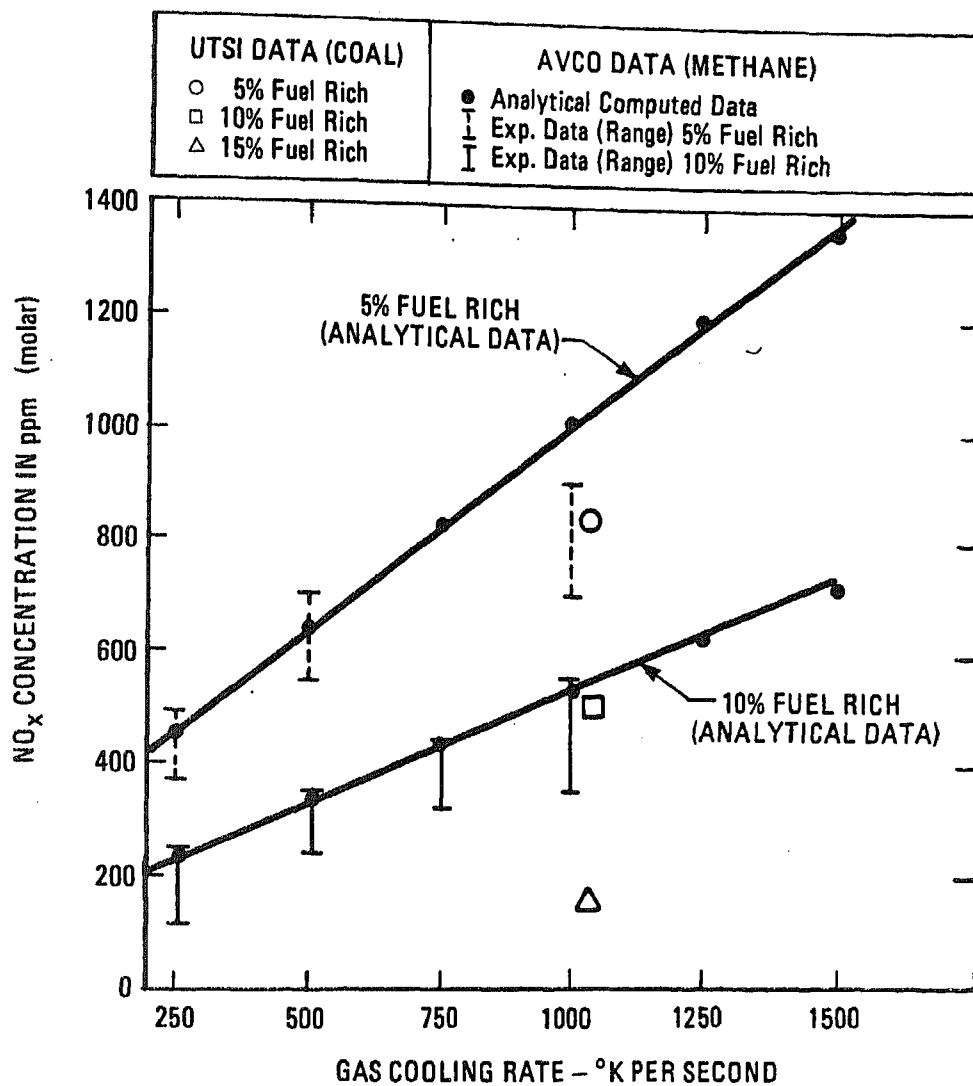
FIGURE 6.   FINAL NO$_x$-CONCENTRATIONS IN MHD-EXHAUST GAS ACCORDING
TO EXPERIMENTAL AND ANALYTICAL DATA (TAKEN FROM REF. 7)

A calculated example is shown in Fig. 4 for 10% fuel-rich (methane) mixture and a constant cooling rate of 500°K/sec; the equilibrium NO concentration is also shown. Figure 5, which is for the case of a sub-bituminous coal, shows calculated curves of NO stack emissions versus gas residence time.[2] The present and proposed NSPS for sub-bituminous coal firing is indicated on Fig. 5.

Early experiments with gaseous fuels by Hals and Lewis, in the appropriate range of temperature and stoichiometry, resulted in excellent agreement with theory.[7] These data, together with recent experimental results from UTSI, are shown on Fig. 6 in comparison with prediction. The calculated curves on Fig. 6 represent the final or near asymptotic NOx concentration as a function of cooling rate for two fuel-rich mixtures. The UTSI data, referred to in Section II of the present paper, were for coal combustion and nearly pure oxygen as the oxidizer.[4-6] The significance of being able to operate at a high cooling rate and simultaneously meeting NOx standards is to reduce the size and, therefore, cost of the radiant boiler.

Limited measurements with coal combustion have been made by Bienstock et al., which indicate that low NOx emission can be achieved by the two-stage combustion process descibed earlier.[15] Results are shown on Table III. These tests were executed at a relatively low combustion temperature (2200°K) and were 33% oxygen enriched. Nevertheless, the results imply the capability to successfully control NOx in an MHD system.

Plant Design

Detailed kinetics-based calculations for NOx emissions have been performed for two representative flow-train conditions.[7] These are shown on Figs. 7 and 8 for the case of 3000 and 2000°F air preheat, respectively, with coal as the fuel at a fuel-air equivalance ratio of 1.1. In both cases, NOx stack emissions meet present and proposed NSPS.

A key matter in radiant boiler design is the determination of boiler size (or height) necessary to achieve a specified value of NOx emission. This question was addressed by Hals et al. for a full-scale, coal-fired MHD/steam plant.[11] The result is shown in Fig. 9, and compared with present and proposed NPS.

In a model developed by Argonne National Laboratory (Ref. 16), the effects of fuel stoichiometry, residence time, NOx chemical kinetics, thermodynamic conditions, and radiant heat transfer on the NOx concentration and the radiant boiler size are taken into account. The ANL calculations are based on simultaneous solution of a set of chemical kinetic and heat transfer equations. The rate constants used in these equations were determined by JANNAF (Joint Army, Navy, NASA, and Air Force Committee), and the chemical kinetics, in turn, are essentially based on the NASA Chemical Kinetic Code. Figures 10 and 11 present typical calculated NOx concentrations using the ANL code as a function of gas residence time in the boiler for stoichiometric ratios of 0.95 and 0.85 respectively. These calculations indicate that the present and proposed EPA NOx emission standards and most state NOx standards may be

TABLE III
PETC DATA

NO$_x$ FORMATION IN 2-STAGE COMBUSTION

First Stage			Second Stage							
Sampling at 3500 - 3600°F			Gas entrance temperature, °F				Effluent concentration			
% Stoichiometric oxygen	NO$_x$ ppm	CO vol. -%	2000	2150	2450	2850	% Stoichiometric	NO$_x$, ppm	$\dfrac{\text{lb NO}_2}{10^6 \text{ Btu}}$	CO vol -%
110	4400	1.14					110	4036	3.13	0
102	2695	2.17					102	2612	2.00	0.1
101	2650	2.27					101	2225	1.70	0.4
95	880	4.30	x				106	150	0.12	0
94	782	6.61		x			103	351	0.27	0
94	727	6.90			x		105	550	0.40	0
92	543	8.11			x		107	575	0.43	0
92	496	7.53				x	107	885	0.65	0
91	496	9.95				x	104	885	0.64	0
88	356	10.40				x	104	814	0.59	0

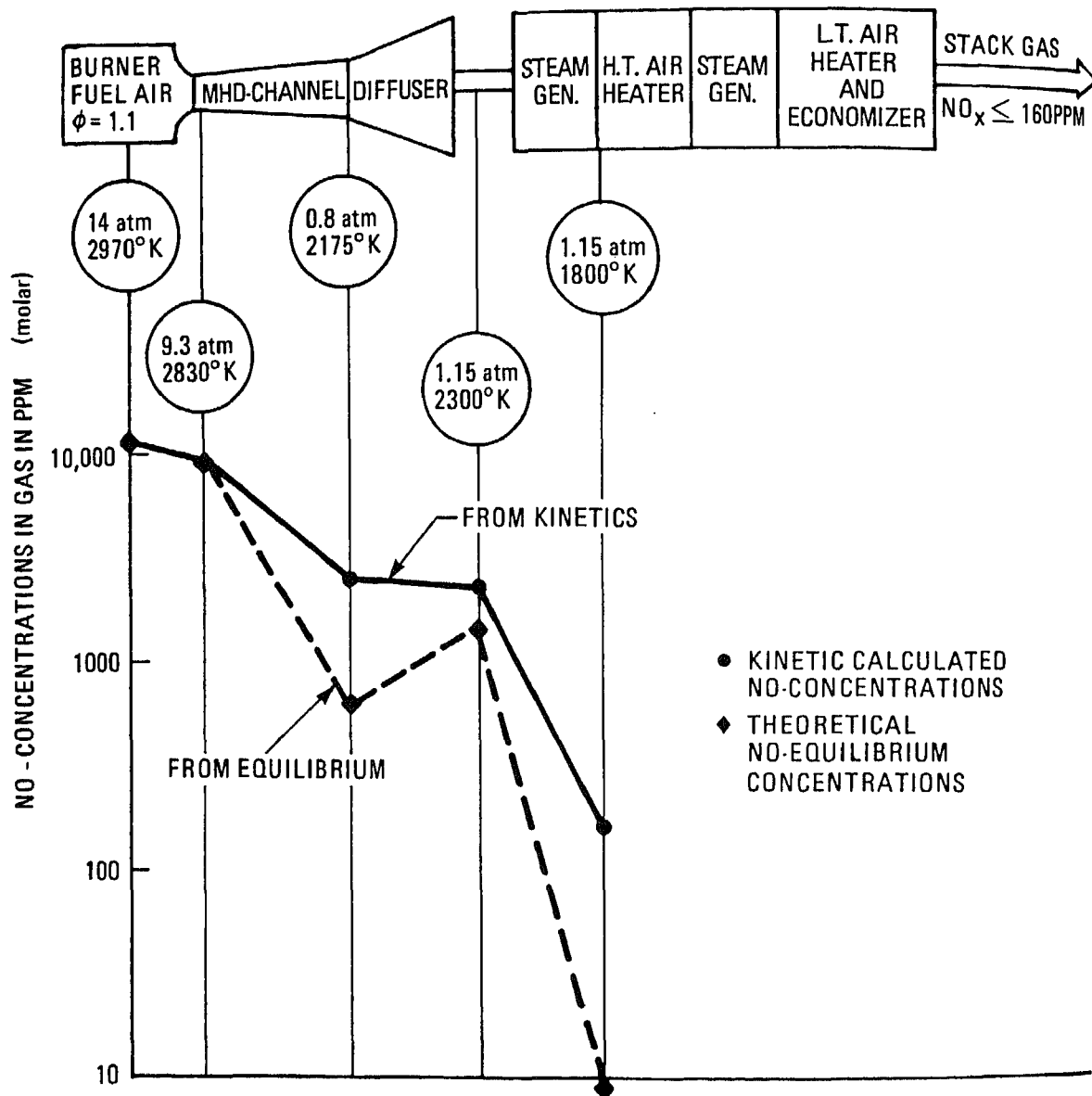(Taken from Ref. 15)

FIGURE 7.   MHD-STEAM POWER PLANT WITH TWO-STAGE COMBUSTION FOR
            CONTROL OF NITROGEN OXIDES.   3000°F ASSUMED AIR PRE-
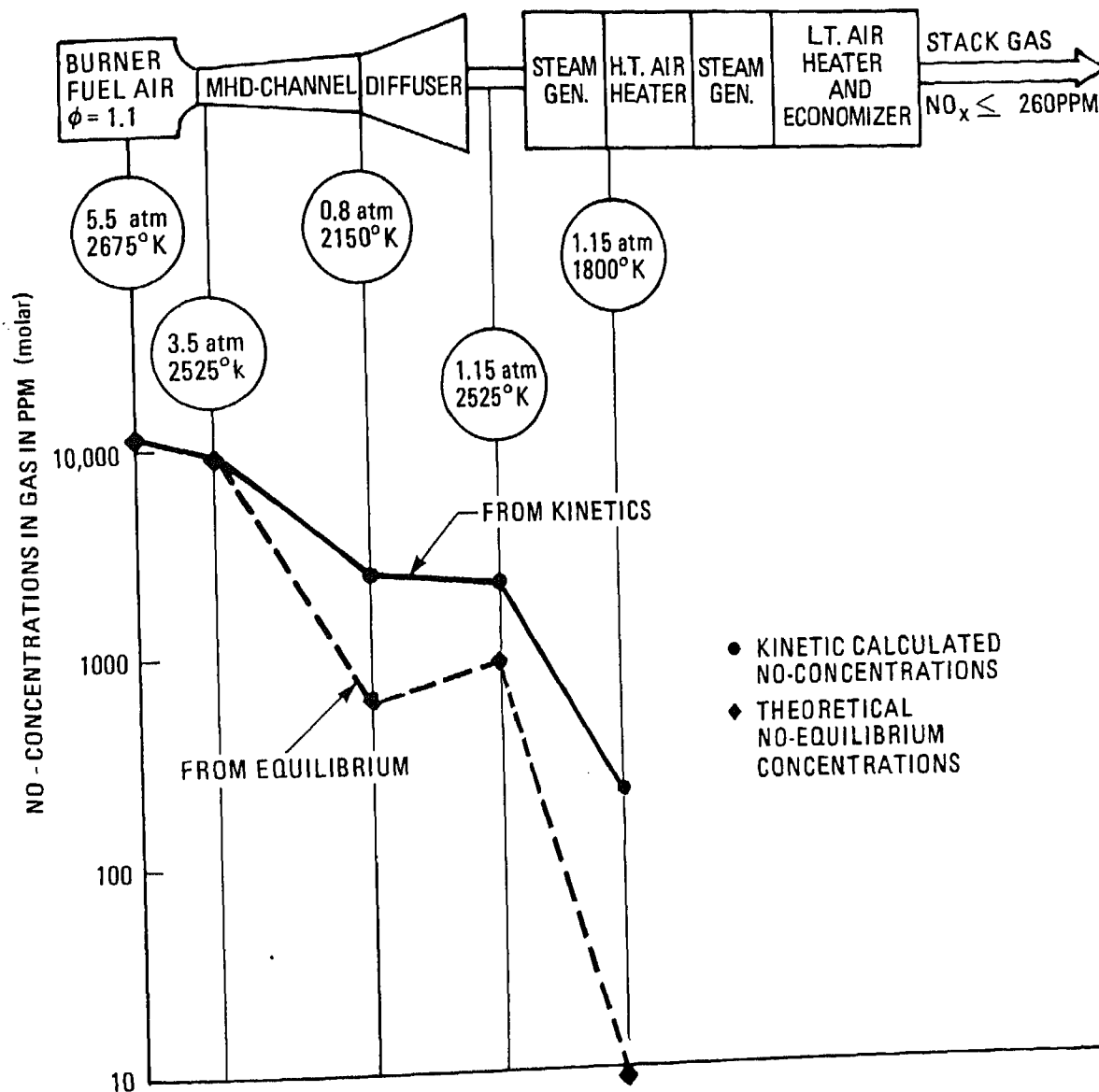   HEAT TEMPERATURE. (TAKEN FROM REF. 7)

FIGURE 8. MHD-STEAM POWER PLANT WITH TWO-STAGE COMBUSTION FOR CONTROL OF NITROGEN OXIDES. 2000°F ASSUMED AIR PRE-HEAT TEMPERATURE. (TAKEN FROM REF. 7)
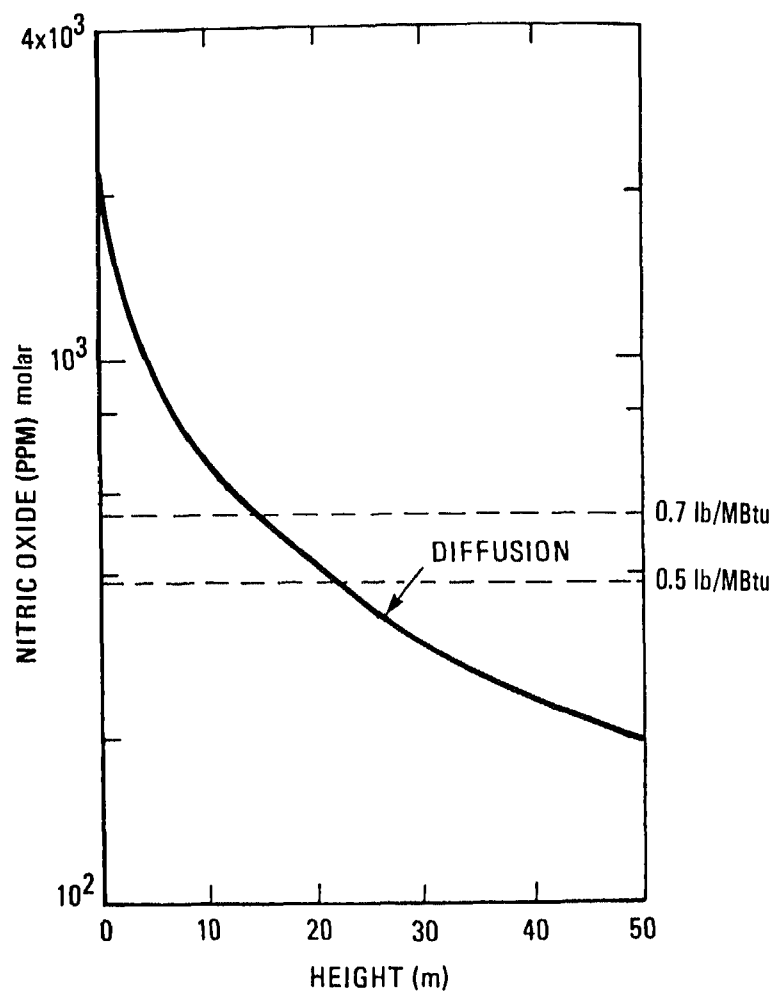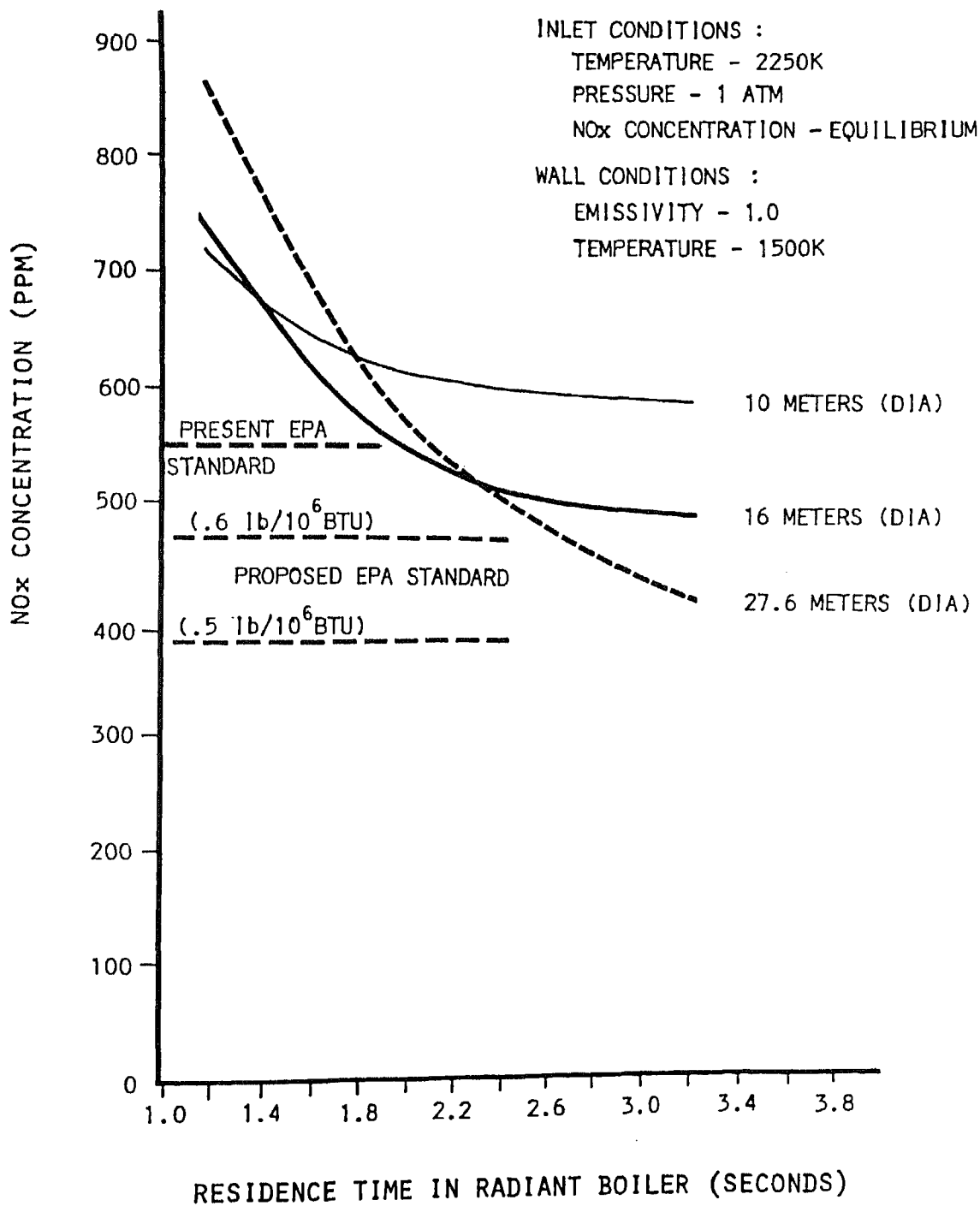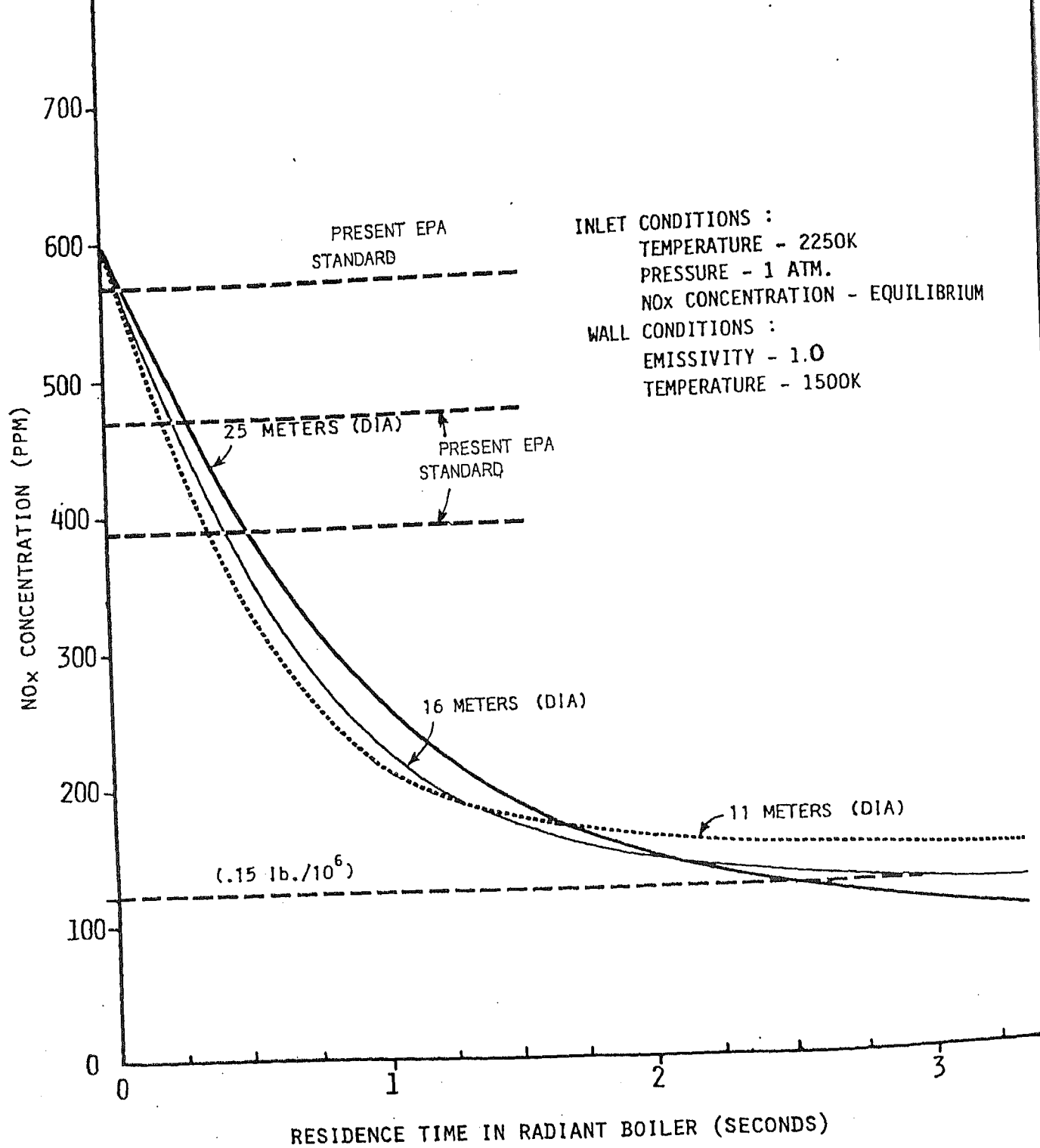
FIGURE 9.   NITRIC OXIDE CONCENTRATION AS A FUNCTION OF HEIGHT
IN A STEAM GENERATOR FOR DIFFUSION PLUS TRANSPARENT
RADIANT TRANSFER.   (TAKEN FROM REF. 11)

(REF. 16)

INLET CONDITIONS :
    TEMPERATURE - 2250K
    PRESSURE - 1 ATM
    NOx CONCENTRATION - EQUILIBRIUM
WALL CONDITIONS :
    EMISSIVITY - 1.0
    TEMPERATURE - 1500K

10 METERS (DIA)

PRESENT EPA
STANDARD

$(.6 \text{ lb}/10^6 \text{BTU})$

16 METERS (DIA)

PROPOSED EPA STANDARD

27.6 METERS (DIA)

$(.5 \text{ lb}/10^6 \text{BTU})$

NOx CONCENTRATION (PPM)

RESIDENCE TIME IN RADIANT BOILER (SECONDS)

INLET CONDITIONS :
    TEMPERATURE - 2250K
    PRESSURE - 1 ATM.
    NOx CONCENTRATION - EQUILIBRIUM
WALL CONDITIONS :
    EMISSIVITY - 1.0
    TEMPERATURE - 1500K

PRESENT EPA STANDARD

25 METERS (DIA)

PRESENT EPA STANDARD

16 METERS (DIA)

11 METERS (DIA)

$(.15 \text{ lb.}/10^6)$

NOx CONCENTRATION (PPM)

RESIDENCE TIME IN RADIANT BOILER (SECONDS)

These figures also show that a decrease in stoichiometry reduces the required size of the boiler for any given level of NOx at the boiler exit. For a stoichiometry of 0.85, for example, NOx concentrations as low as 0.18 lbs/10^6 Btu can be attained when a 35 ft. diam. boiler with 3 second residence time is selected. For a 500 MWt power level, this would require a boiler height of 97 ft. Boiler dimensions in this range are quite reasonable. The corresponding gas velocity is 36 ft/sec which is within the limit of velocities employed in conventional boiler designs.

Note that in the above example, the NOx concentration is three times lower than the September 11, 1978, proposed EPA standards (Ref. 14). Moreover, the NOx level which may be achieved approaches very closely the most stringent state standard which has been proposed (California: 0.15 lb NOx/10^6Btu). Ultimately, selection of optimum stoichiometry and boiler size would be determined by the corrosion characteristics of candidate boiler materials, cost tradeoffs and the prevailing Federal or local NOx standards. However, it is of interest to note that, as shown in the joint ERDA-NASA-NSF Energy Conversion Alternative Study-ECAS, variations in size of the radiant boiler do not result in appreciable changes in MHD plant costs.

The above calculations are supported by the experimental results on NOx emissions measured at the University of Tennessee Space Institute (UTSI) (Ref. 4-6) and by the Pittsburgh Energy Research Center (PERC) (Ref. 15). Experimental results obtained in their coal-fired MHD-type test units are summarized in Fig. 12. Both the reduction in the NOx concentration with decrease in stoichiometry and the very low NOx concentration at 0.85 stoichio-metry are consistent with the calculated results shown in Figs. 10 and 11. The experimental results provide a reasonable validation of the ANL computa-tional model. The model appears to predict slightly conservative NOx levels but within the scatter of the experimental data. In any event, experimental data from several laboratories confirm that NOx emissions from MHD systems may be kept within existing and proposed standards, and that reasonable pre-dictive and scaling models are available.

It should be noted that the results in Figs. 10 and 11 do not include the effect of particle radiation. A model which takes particle radiation into account is currently under development. Preliminary results show that particle radiations would require larger size boilers but not to the extent of affecting the above conclusions.

RATIO OF OXIDANT TO THEORETICAL OXIDANT
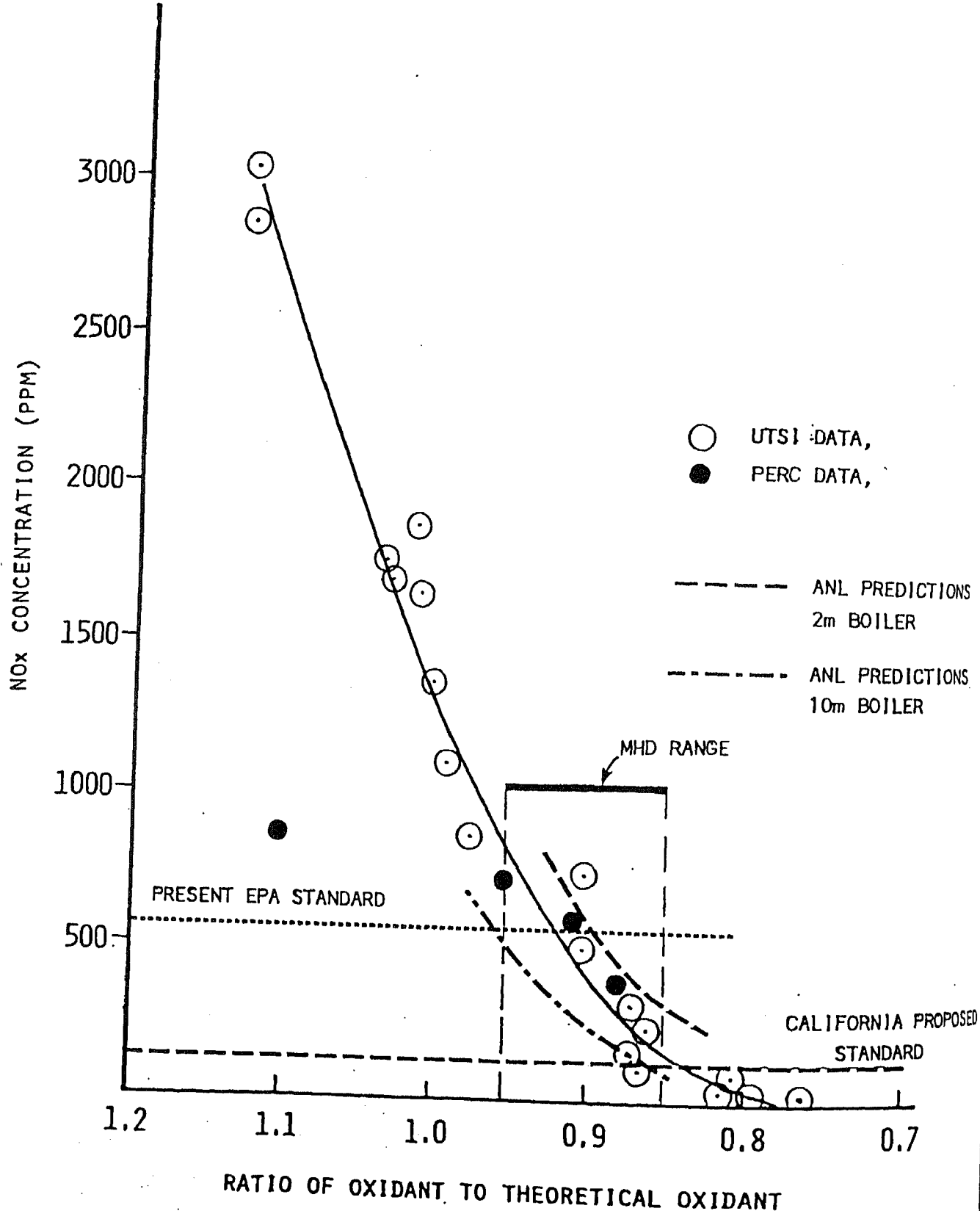
mate concern for coal-fired MHD/steam power plants. Analytical and experimental investigations have been underway since the early 1960's. These efforts have served to identify the radiant boiler as the key component in MHD NOx control. The preferred system operation is to: (a) operate the combustor fuel rich; (b) cool the gas slowly in the radiant boiler; and (c) add additional downstream air to complete combustion.

Present and proposed NSPS for NOx emissions can be met by the above-mentioned technique. The MHD Division of DOE has devised and is implementing an Environmental Development Plan (EDP) to identify and schedule further, appropriate NOx Research and Development. Current DOE-sponsored development efforts are aimed at optimizing the method and at formal demonstration in suitable facilities. A noteworthy example is the Coal Fired Flow Facility (CFFF) at the University of Tennessee Space Institute (UTSI) which is scheduled to operate in CY'79.

Contributors

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1. INTRODUCTION

A major objective of the U.S. effort to develop coal-fueled, open-cycle MHD electrical power generation for utility application is to assure that future MHD plants can meet the most stringent existing and anticipated Federal, state and regional emissions requirements for sulfur oxides (SO_x), nitrogen oxides (NO_x) and particulate matter. In addition, although emission standards presently do not exist, it is necessary to give careful attention to the emission potential for; heavy or trace metals, materials having a carcinogenic potential and other substances which may have adverse health effects. All new energy conversion methods must effectively control the emissions of all of these substances, not only by today's standards, but future standards as well.

To achieve this goal in the coal-fired MHD development program, a technology base is now being established through conduct of experimental programs with subscale MHD components and systems using various domestic coals but primarily those of high sulfur content. Current subscale tests in MHD facilities are providing test data on the emissions and control of SO_x, NO_x, solid particulate matter and heavy metals. In addition, a test program to assess the emissions of substances having a biological impact is being planned.

The purpose of this paper is to discuss control of (1) SO_2, (2) particulate emissions, and (3) potentially toxic substances in MHD systems, and to review some accomplishments in MHD environmental control technology development. The control of NO_x emissions is discussed in a companion paper (Ref. 1). Finally, an assessment of environmental control and potential emissions from MHD commercial plants is presented.

2. EMISSION REQUIREMENTS

Table 1 summarizes air emission standards required by 1) EPA (present and proposed), 2) representative states across the U.S., and 3) some of the most demanding environmental control areas in the U.S. Projected emission levels from a future MHD steam power generating plant, which can be projected at this time, are also shown.

As summarized below, a principal emission from an MHD plant will be very small particulate sulfates. At the present time, there are neither ambient air nor emission standards for sulfates. Ambient standards are being discussed

	NO$_x$ (lb/mm BTU)	Particulates (lb/mm BTU)	SO$_2$ (lb/mm BTU)
Federal Standards			
EPA (present, Ref. 4)	0.7	0.1	1.2
EPA (proposed, Ref. 5)	0.5 (Sub+Bitum)	0.03	0.2 or 85% reduction
State Standards			
Montana	0.7	0.2	1.0
Tennessee	0.7	0.1	1.2
Massachusetts	0.7	0.1	1.2
New Mexico	0.45	0.02	0.34
Illinois	0.7	0.1	1.2
California (proposed)	0.15	0.005	0.7
California (L.A. Basin)	0.08*	0.0058*	0.117*
MHD Facilities			
Current Experimental Results	0.15	0.026	.66 (1) .04 (2)
Projected for Commercial Plant	0.15	0.01	95% reduction

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* Calculated for Total Emissions of a) NO$_x$ = 140 lb/hr
b) Part. = 10 lb/hr
c) SO$_2$ = 200 lb/hr

For a plant of 500 MW at 50% efficiency using coal with 4% sulfur and 13% ash and having a heating value of 12,000 BTU/lb.

(1) 90% reduction using 1% seed and 4% sulfur coal
(2) 90% reduction using 1% seed and 0.5% sulfur coal

are primarily produced in the atmosphere rather than emitted from particular sources (Ref. 3).

Future restrictions on the emissions of substances having carcinogenic potential, toxic substances and heavy metals may be expected. However, so little is known about the special problems associated with the emission of toxic substances and carcinogens that it is not possible to make a definitive assessment of future emission limits.

3. OPEN-CYCLE MHD SYSTEMS

The major focus of MHD power system development in the United States is the open-cycle system, where high-temperature combustion gases are directly utilized as the MHD topping unit working fluid to produce electricity and subsequently used to produce additional power in a steam bottoming plant. The various components and a schematic arrangement of an MHD open-cycle plant are given in Fig. 1 and some details of the operation of key components are presented in Ref. 1 as they relate to the control of NO_x.

Inherent in the overall MHD open-cycle process is also a mechanism which permits the control of SO_2. This mechanism is an integral part of the fundamental physical and chemical processes occurring within the MHD power generator and in certain downstream subsystems. Thus, control of SO_x in MHD systems does not involve "add-on" control systems such as flue-gas scrubbers in conventional plants. Those regions or components in the bottoming plant in which NO_x, SO_x and particulate control is carried out are also illustrated in Fig. 1.

In the MHD power generation system the combustion process is achieved at approximately 5000°F in order to the necessary electrical conductivity in the MHD generator. These high combustion temperatures are also responsible for the high plant thermal efficiencies of MHD systems, and significantly reduced thermal emissions over those of conventional plants. In addition, the high temperatures achieved in the MHD combustor will serve to break down carcinogenic or toxic compounds into simpler substances. These compounds could reform at lower temperatures as the combustion gases coal. The existence of higher temperatures should increase the heavy metal emissions because a larger fraction will be vaporized and carried over and through the bottoming plant boiler.

4. SO_x EMISSIONS AND CONTROL

A major advantage of the MHD power generation system lies in the fact that the alkali metals used to seed the combustion gases to increase electrical conductivity and make the MHD process work also interact with the gaseous sulfur compounds converting them to a solid form. Thus, as an integral part of the MHD process, potassium seed material added at the combustor results in the formation of liquid or solid potassium sulfate in the flue gases, which may be subsequently removed in downstream components. This is a very efficient gas-phase reaction resulting in very significant reductions of the SO_2 emissions.

FIGURE 1 MHD SCHEMATIC – COAL FIRED SEPARATELY FIRED PREHEATER
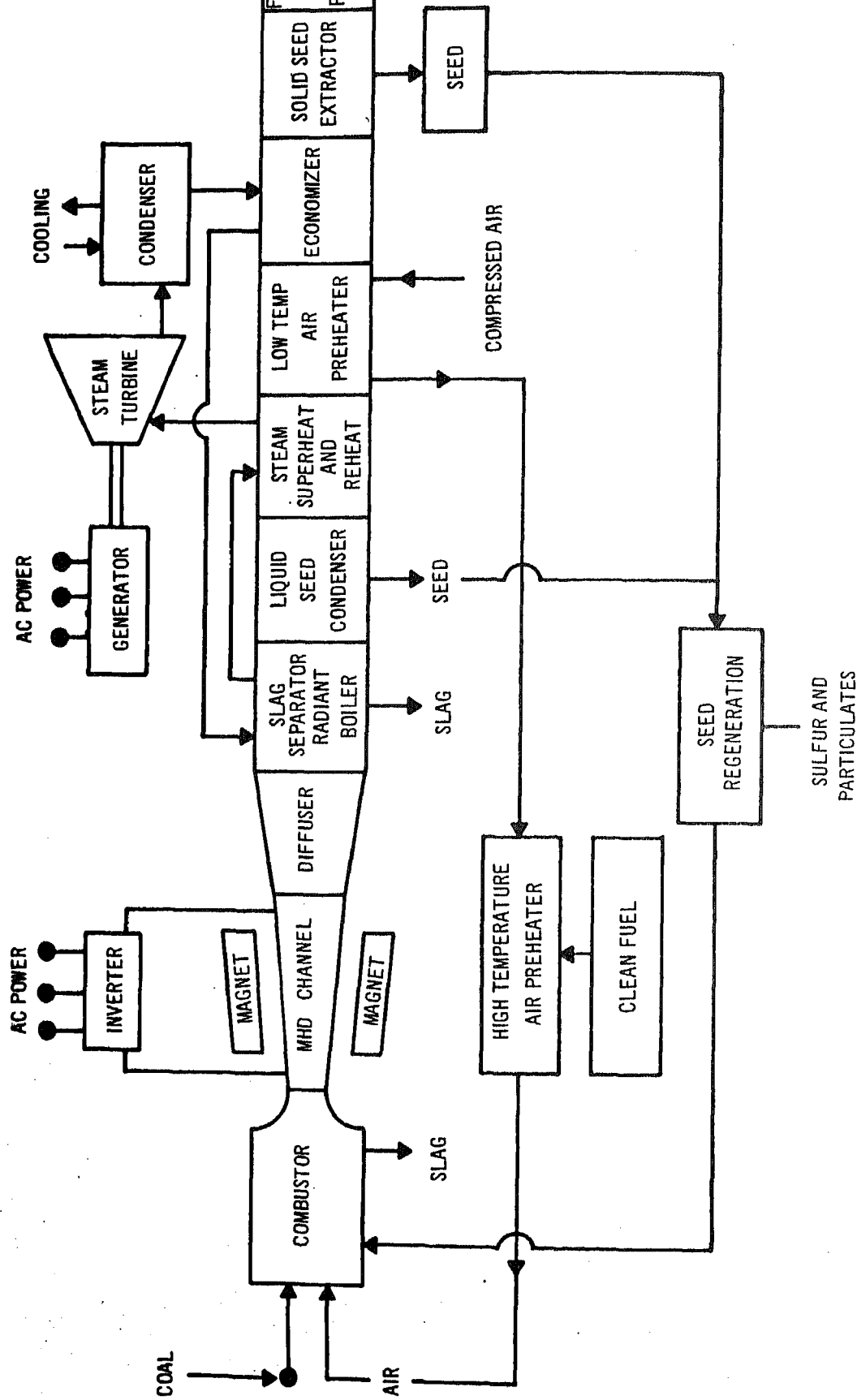
of the plant indicated in Fig. 1. In an MHD plant, the potassium sulfate must be collected at several points and reprocessed to K_2CO_3 for return to the combustor as seed. In the reprocessing the sulfur may be removed as (1) H_2SO_4, (2) elemental sulfur, or (3) as a waste product.

The sulfur chemistry which will occur in MHD plants has been studied by several groups. A model developed by Argonne National Laboratory (ANL) for the prediction of sulfur oxide concentration in MHD systems is based on the assumption that the condensed species in the gas-seed-slag system are in chemical equilibrium. Thermodynamic data used in calculations with this model are obtained from the JANAF tables and from experiments at ANL. Figure 2 shows, for conditions in an MHD bottoming plant, the ratio of the sulfur in the gas phase to the total sulfur input as a function of temperature, for various amounts of potassium seed material added to the system and for a stoichiometry of 0.9. It can be seen from this figure that K/S ratios larger than 1.8 will result in a 90% reduction in sulfur content in the stack flue gases. This means that 1% by weight potassium in the gas (a typical MHD system operational condition), can remove 90% of the sulfur for coals having a sulfur content as high as 4.5%. The use of more potassium seed than that needed for MHD purposes would allow the use of higher sulfur coals.

These theoretical results are supported by experiments conducted at the Pittsburgh Energy Research Center (Refs. 6 and 7) and at the University of Tennessee Space Institute (Ref. 8) which experimentally show the effectiveness of potassium in removing sulfur from the flue gas. In Fig. 3, the measured SO_2 emissions from the coal-fired MHD-type facilities are plotted as a function of the ratio of the potassium added to the amount of sulfur in the coal in terms of the K/S ratio. The coal sulfur content in these tests varied from 2.5 to 4.5%. Figure 3 indicates that when the K/S ratio is 2.2, SO_2 emissions are reduced by 90%. With 1% K (by weight in the gas), 90% SO_2 reduction could be attained for coals with sulfur contents as high as 4%. The experimental tests have shown that between 85% and 95% of the potassium/sulfur stoichiometry for the formation of K_2SO_4 is achieved. Thus, this SO_2 control process is much more effective than most of the flue-gas desulfurization processes which would be needed for conventional plants. SO_2 reductions greater than 90% may be achieved by the use of added potassium.

The discrepancy between these experimental results and the results from the equilibrium calculations is due to the differences in the amount of slag carryover. The calculations given in Fig. 2 were also performed for Rosebud coal with 10% ash carryover. In contrast, the experimental results shown in Fig. 3 were measured under the conditions where 100% of the ash from Eastern coal was carried through the system. Nevertheless, the calculational model and experimental tests at two laboratories confirm that MHD systems will operate with low SO_x emissions that will be well within the present Federal and all state standards, as well as the proposed EPA SO_2 emission standard. Introduction of larger amounts of seed components can permit the use of the

FIGURE 2 SULFUR GAS AS A FRACTION OF TOTAL SULFUR
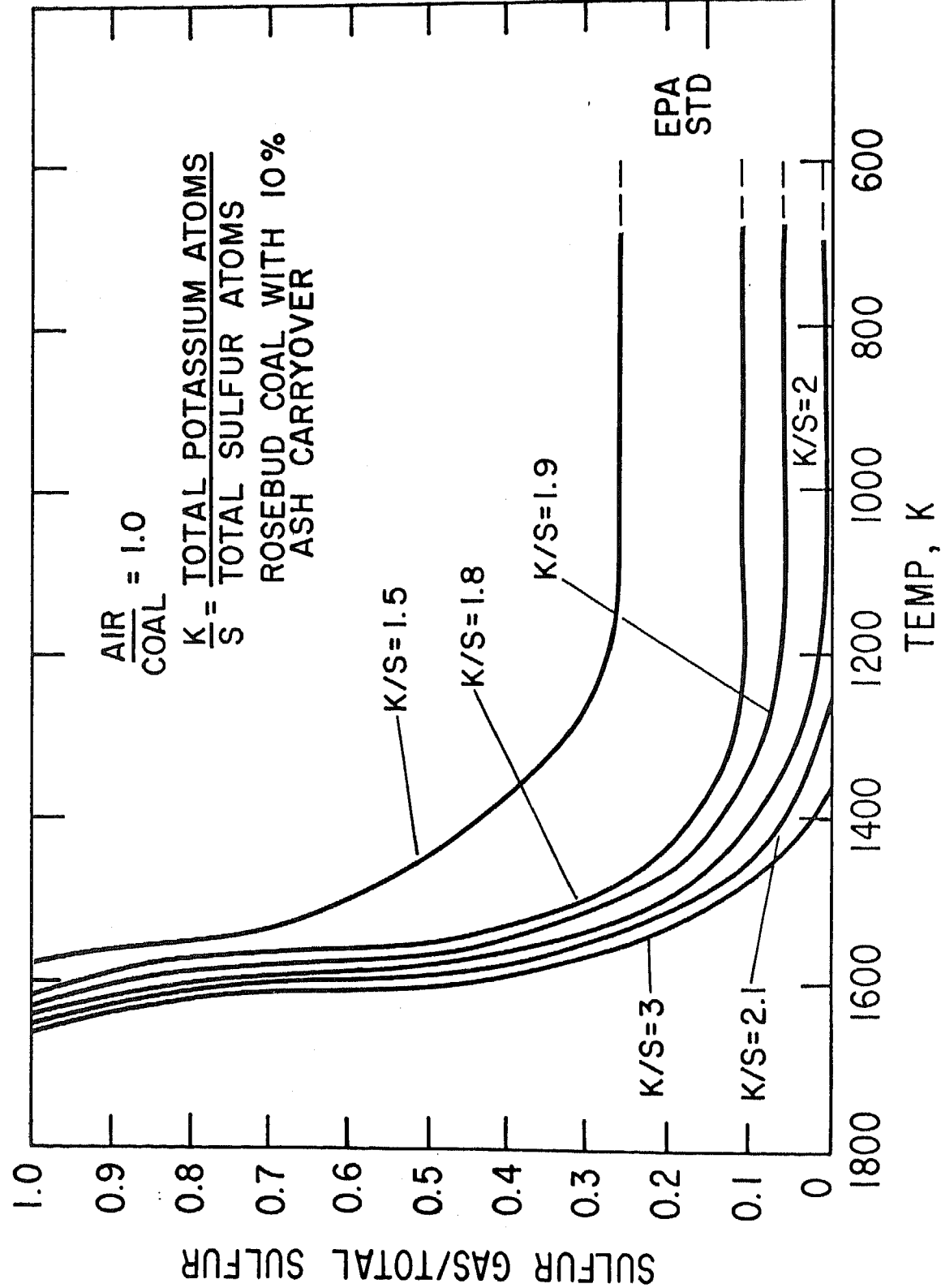
As noted above, the experimental result from Refs. 6 and 8 indicate that for a potassium to sulfur ratio of 2.5 (which corresponds to the stoichiometric ratios for the formation of potassium sulfate), approximately 10 to 20% of the potassium was not utilized to form solid potassium sulfate. This potassium most probably became bound in other compounds such as potassium silicate and, therefore, was not available to react with the sulfur in the system. This has two detrimental effects; first, the potassium forms water-insoluble compounds, which complicate the reprocessing of the seed, and second the potassium becomes unavailable to react with SO_x in the system.

At 100% ash carryover, as confirmed by equilibrium relations and analytical models, slag at 1700 K will contain 15% (by weight) potassium. Therefore, with 10% carryover for a typical eastern coal (15% slag), 0.15 lbs of slag will contain 0.00225 lbs of potassium. Since approximately 0.1 lbs of potassium for each pound of coal entered the system, the total loss of potassium would be approximately 2%. Results from independent material mass balances confirm this point. Moreover, recent experiments with 10% ash carryover simulation in the U.S.S.R. resulted in a seed loss of 2% as predicted above. The implication is that potassium losses can be kept low in MHD systems and hence SO_2 control effectiveness will remain high.

4. PARTICULATE EMISSIONS AND CONTROL

As mentioned above, combustors in MHD systems must operate at high temperatures in order to achieve the necessary electrical conductivity in the potassium-seed combustion gases. In one MHD system concept up to 90% of the coal slag will be tapped from the combustor exit before the seed is added (see Fig. 1) in order to minimize the potassium loss to the slag and because only a small amount of slag is needed to coat the walls of the MHD generator. In another concept, all of the slag would pass through the generator and a large portion then removed from the radiant boiler. In either case, the high combustion temperatures result in a major portion of the mineral content of the coal being vaporized. Consequently, the ash carryover will produce flyash with a different composition and having a much smaller particle-size distribution than occurs in a conventional utility boiler. Slag and flyash will be taken from various points of the system as shown in Fig. 1.

The chemical composition of slag and flyash varied widely and depends on the coal burned, the mining and processing methods and the degree of coal cleaning before burning. Table 2 compares some typical measured compositions (in terms of equivalent oxides) in conventional boiler and MHD systems. It is apparent that both silicon and aluminum will be selectively rejected at the combustor exit and that MHD system flyash has a different composition than that from conventional plants. In particular, it will be rich in potassium sulfate for the reasons outlined in the previous section.

Figure 4 compares SEM micrographs of flyash from a conventional plant (Ref. 9) with that obtained from an MHD system (Ref. 10). The spotted coating on the surface of the MHD flyash is K_2SO_4, illustrating that the flyash particles serve as nuclei upon which potassium sulfate condenses. Also, as
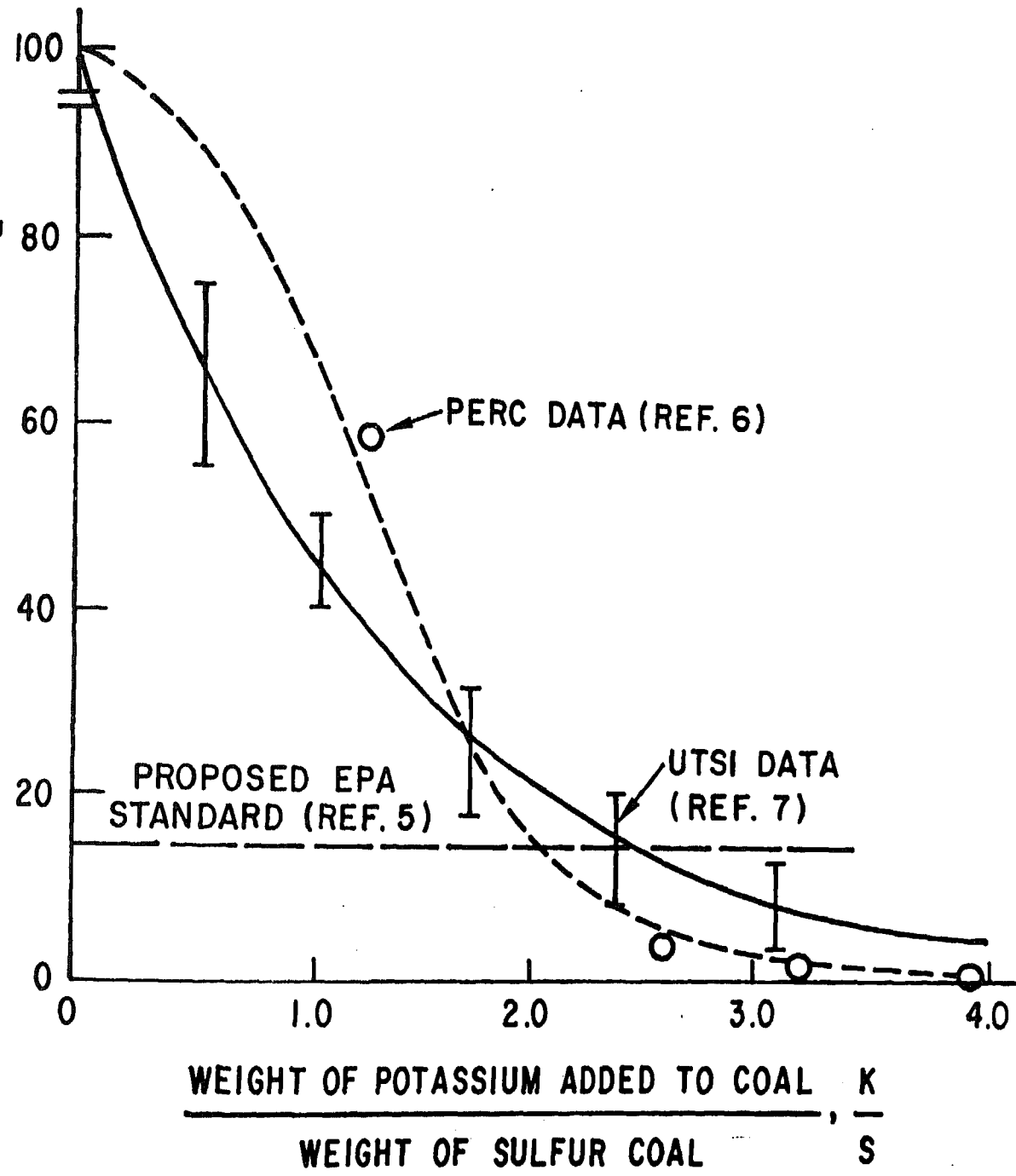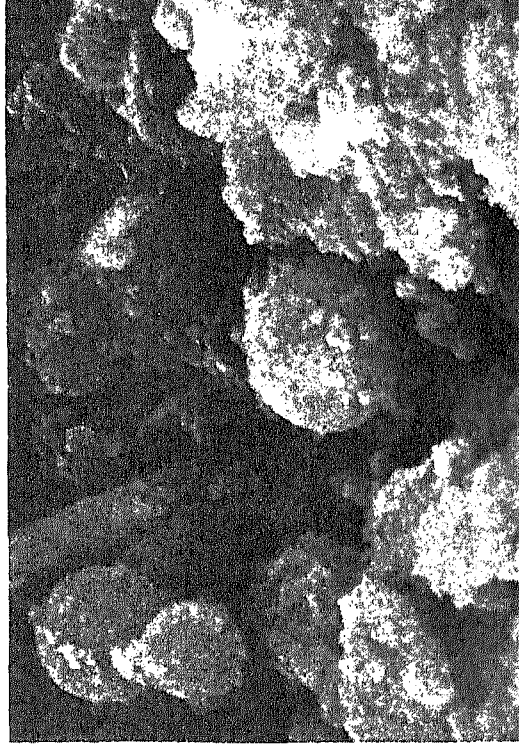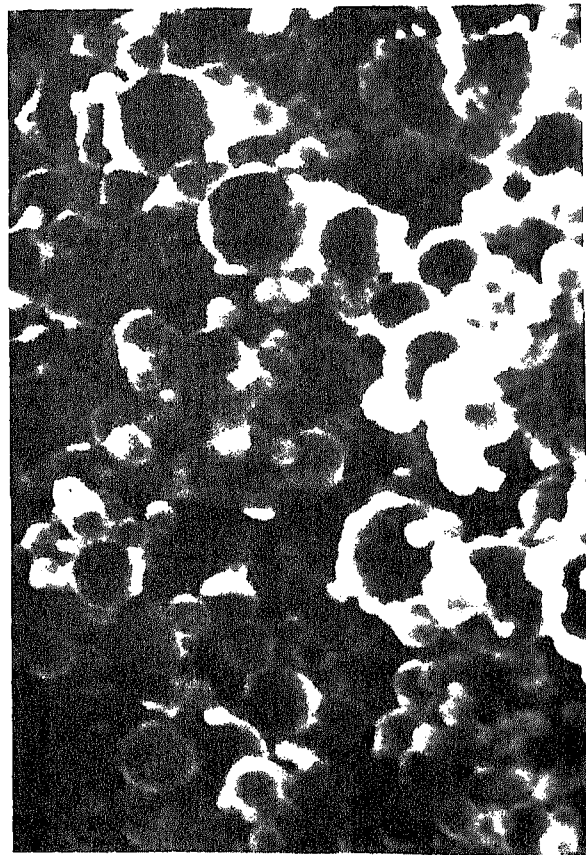
Table 2

Comparison of Slag and Flyash from Conventional Boiler and MHD Systems (Eastern Coal)

Compound	Conventional Coal-Fired Boiler (Ref. 9)	MHD Coal-Fired System (Ref. 10)	
	Flyash	Combustor Slag	Flyash
SiO_2	39.80	40.42	23.56
Al_2O_3	21.20	27.01	14.00
Fe_2O_3	24.70	10.41	9.81
CaO	4.55	2.60	1.50
Na_2O	0.28	0.70	0.78
C	-	0	5.91
CuO	-	0.06	0.23
K_2SO_4	-	3.05	38.23
K_2O	2.25	0.05	-
MgO	1.04	5.0	3.0
TiO	1.24	1.0	0.8
P_2O_5	0.31	0.4	0.4
Moisture	-	0.1	0.5
SO_4	0.72	0	0.60

Y-axis label: FRACTION OF SO₂ EMISSIONS, % = GAS CONCENTRATION OF SO₂ / INITIAL SO₂ CONCENTRATION

Chart labels:
- PERC DATA (REF. 6)
- UTSI DATA (REF. 7)
- PROPOSED EPA STANDARD (REF. 5)

X-axis label: WEIGHT OF POTASSIUM ADDED TO COAL / WEIGHT OF SULFUR COAL , K/S

DUST COLLECTED BY CYCLONE WITH K_2SO_4
5000X MAGNIFICATION

FIGURE 4   COMPARISON OF SEM MICROGRAPHS OF FLYASH FOR MHD SYSTEM AND
CONVENTIONAL COAL FIRED SYSTEM.

However, some additional studies indicate that the mean size of MHD flyash is in the range of 0.2 to 0.5 microns. Assuming a mean size of 0.3 microns, a reasonable estimate of the size distribution of flyash in an MHD system is also sketched in Fig. 5, which may be used to make estimates of the collection effectiveness of conventional particulate control equipment.

There is also some experimental evidence (see Table 3 and Ref. 13) obtained in small-scale facilities, that indicates that the magnetic field in MHD generators may also have an influence on the formation of particulate matter. The presence of a magnetic field appears to result in the formation of a larger number of submicron particles. At this point, one can only speculate about the reasons for this phenomenon. It may be that the magnetic field suppresses turbulence and/or retards the nucleation point for particulate formation. The consequence of either or both of these phenomena is to decrease the time available for the growth or conglomeration of large particles.

As shown in Fig. 1, coal ash and seed are removed from the MHD system at several points. In a typical MHD system, about 90% of the slag will be rejected at the combustor exit. Small scale tests and calculations indicate that about 2/3 of the remaining 10% of the slag which will be carried into the system will condense in and be removed from the radiant boiler. In addition, between 65 and 85% of the potassium sulfate formed in the bottoming plant will condense and be removed by the seed condensers. Thus, the result is an MHD system using coal with 15% ash and 1% potassium seed and rejecting slag and condensed K_2SO_4 as typically outlined above will pass 1.3 to 3.0 lbs/10^6 Btu of solid particulate into the tail-end gas clean-up system. This material will be made up of fine particle flyash coated with K_2SO_4 with a weight ratio of about 65% K_2SO_4; 35% slag flyash (see Ref. 10) and with a size distribution similar to that shown in Fig. 5.

Wet scrubbers, electrostatic precipitators and baghouses have all been considered for particulate control in MHD systems. Water scrubbers inititally appeared attactive because of the high water-solubility of potassium sulfate. ESP's are considered due to their wide-spread use in the utility industry and baghouses are of interest because of their higher collection efficiency for small particles. Performance characteristics of these three particulate control systems taken from Ref. 14 and 15 are given in Fig. 6 for typical operating conditions of these units in industrial applications. The applicability of these conditions to MHD systems deserves some comment.

An MHD system has been operated while discharging into a baghouse having an air to cloth ratio of 6:1; so Fig. 6(a) is representative of MHD applications. The pressure drop range shown in Fig. 6(b) for venturi scrubbers may be higher than that required for MHD systems; consequently, performance calculations given below for scrubbers may be optimistic. For the case of electrostatic precipitaators, the operational temperature of 310°F and specific collection area (SCA = 285 ft^2/1000 scfm) are quite reasonable for MHD plants. The corona current density at spark breakdown is a function of the flyash resistivity
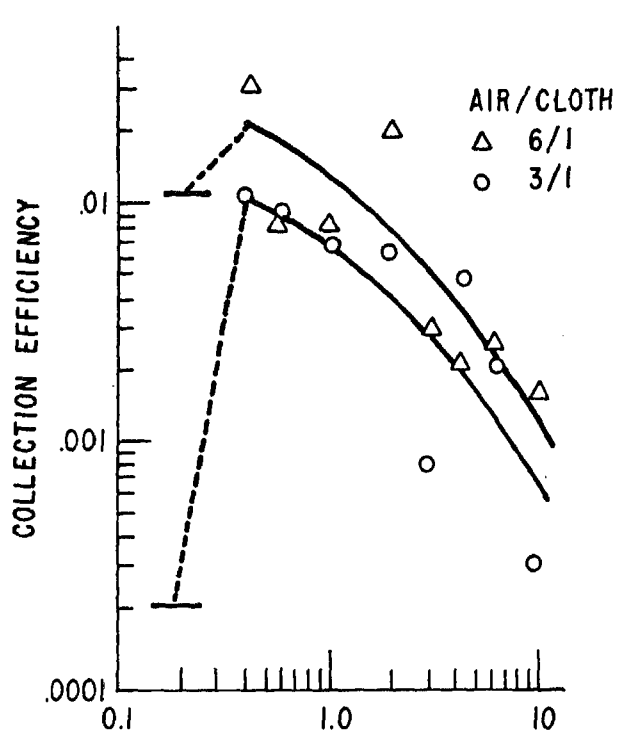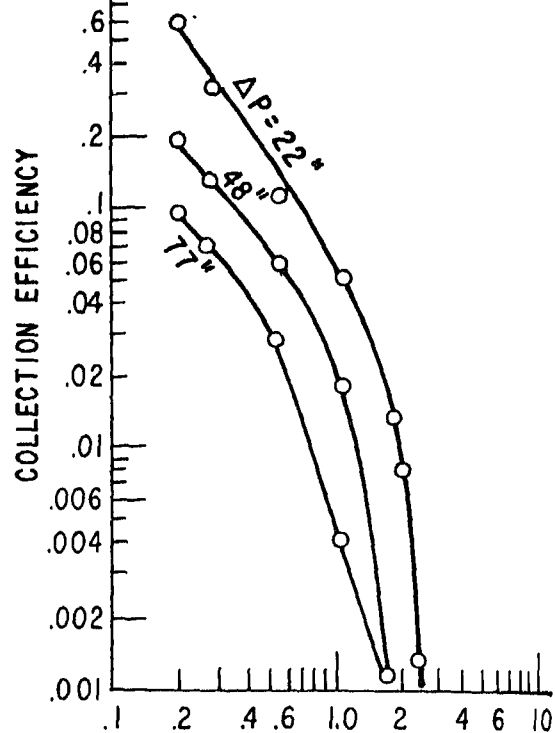
FIGURE 5 PARTICLE SIZE DISTRIBUTION
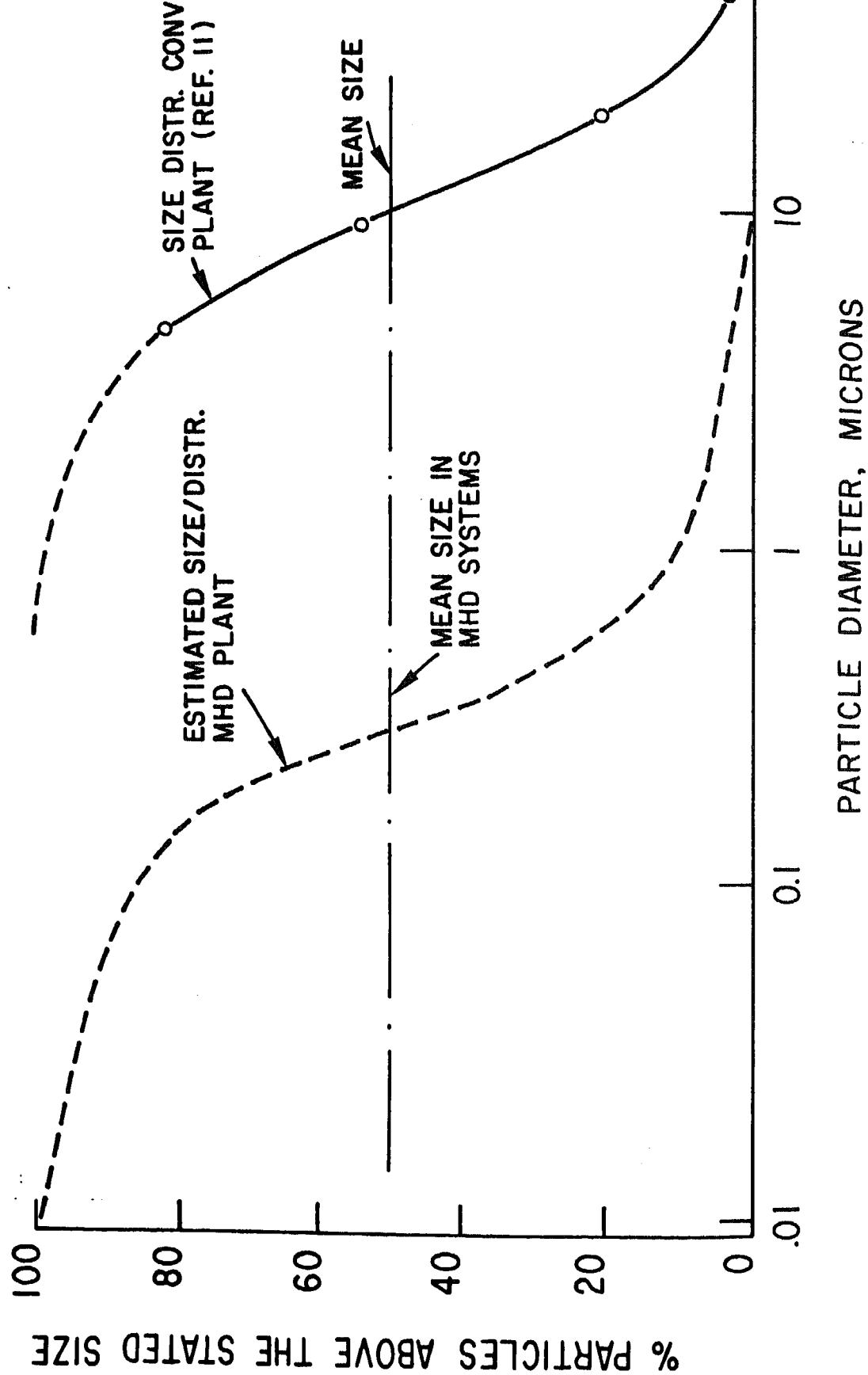
Sample Location		No Magnetic Field	2 T Magnetic Field
Filter	①	15.17% K (wt)	14.53% K (wt)
Water Impinger #1	②	145 ppm	690 ppm
Water Impinger #2	③	42 ppm	108 ppm
Water Impinger #3	④	25 ppm	54 ppm

IMPINGERS

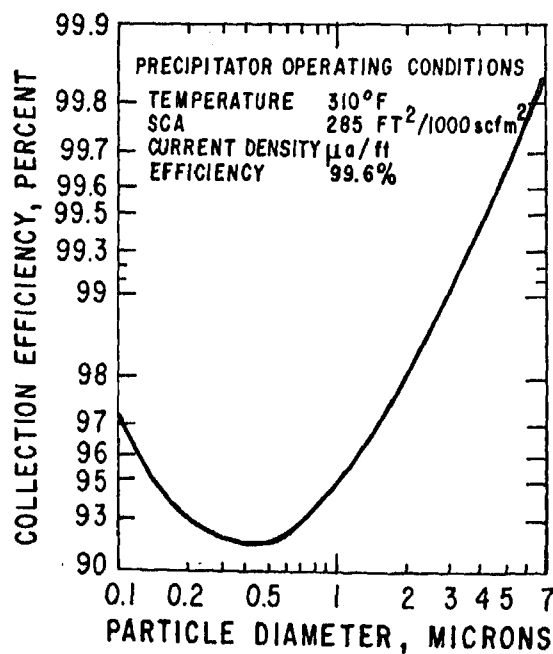STACK   FILTER   #1   #2   #3   EXHAUST
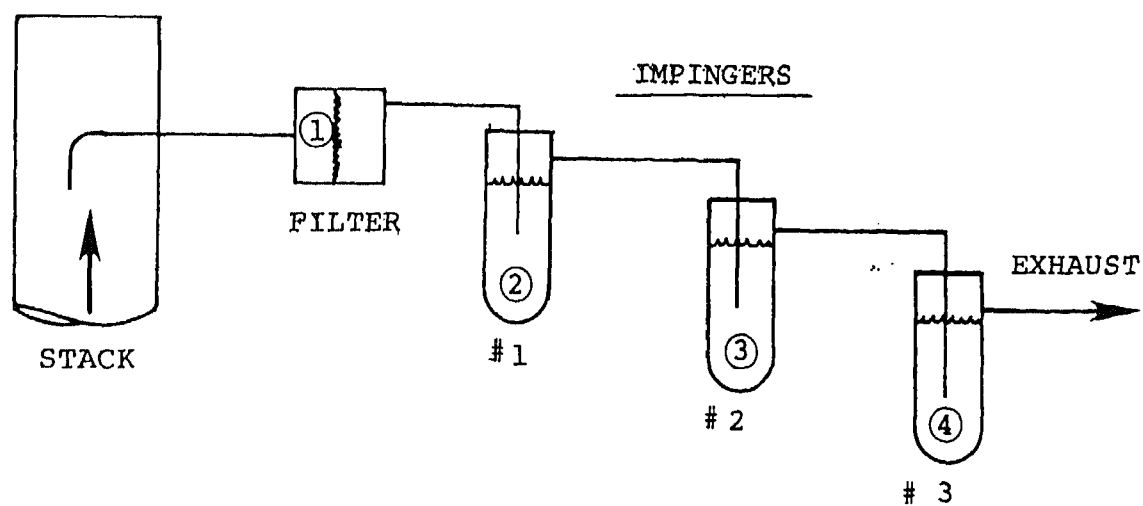
(A) BAGHOUSE (REF. 14)

(B) SCRUBBER (REF. 14)

(C) ELECTROSTATIC PRECIPITATOR (REF. 15)

equivalent to the situation in an MHD system; thus, the ESP performance character-istics in Fig. 6(c) are reasonable for MHD systems.

Using the collection efficiency data in Fig. 6 and the particle-size distribution for MHD flyash in Fig. 5 one can estimate particulate emissions for MHD plants based on the particulate control system operational parameters stated on Fig. 6. For 2.5 lbs/10^6 Btu of flyash passing into the particulate control unit,* particulate emissions from MHD plants would be approximately:

1. Baghouse
   (Nomex bags; air/cloth = 6/1   0.023 lbs particulate/10^6 Btu

2. Electrostatic Precipitators
   (310°F, SCA = 285 ft^2/1000 scfm   0.110 lbs particulate/10^6 Btu
   Flyash resistivity $\approx 10^{11}$ ohm-cm)

3. Venturi Scrubber
   (77" H$_2$O pressure drop   0.156 lbs/particulate/10^6 Btu
    90% K$_2$SO$_4$ washed out)

It is observed that the particulate emission levels for baghouses and ESP's are within current EPA and many state particulate emission standards. Further, baghouses may reduce particulate emissions to within the proposed EPA standard.

While the prospects for particulate collection are good, the utility of ESP units and baghouses in MHD plants needs further examination because of the nature of the alkali-base flyash. For example, elimination of SO$_3$ and other sulfur compounds from the flue gases may increase the resistivity of the flyash beyond that assumed in the above calculation and decrease the performance of electrostatic precipitators (Refs. 12 and 16). On the other hand, the presence of large quantities of potassium will serve to enhance ESP performance (see Ref. 16). Blinding of bags by this hygroscopic material could also present a problem in the application of baghouses. The selection of the optimum particulate cleanup equipment will be governed by the (a) corrosion characteristics of the flyash, (b) the size distribution and composition for a particular type coal, (c) cost tradeoffs and (d) prevailing Federal and local particulate emission standards.

The limited experimental information available on particulate emission control in MHD systems, confirms the above assessment. The only known particulate emission measurements have been made at the University of Tennessee (Ref. 17) using a commercially-available pulsed-air type baghouse. Nomex bags with an air to cloth ratio of 6 to 1 were used. The baghouse operated at a temperature of 400°F and with an inlet grain loading of roughly 1 grain/scf. It is not known, however, if the test operation was of sufficient length to determine whether the bags would be blinded. At these conditions, the particulate emission levels from the baghouse were in the range of 0.01 to 0.03 grains/scf (Ref. 17). For the conditions at which these tests were conducted, an emission grain loading

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* This is in the upper range of particulate loadings estimated above for MHD plants.

tends to support the stated measured values... ...and the reported measurements in MHD systems in which electrostatic precipitators or water scrubbers were used as a particulate control measure.

5. HEAVY METAL AND CARCINOGENS

Table 4 summarizes some representative heavy-metal emissions for large coal-fired utility boilers operating with Eastern coal, and the boiling temperatures for these materials. Because of the higher combustion temperatures in MHD systems, a larger fraction of the heavy metals would be vaporized and may ultimately be emitted into the air. This effect may be evident in the data in Fig. 4 comparing the composition of flyash in conventional and MHD systems. While the initial composition of the coal was different, it is of interest to note that MHD flyash appears to contain fewer heavy metals. A program to determine the heavy-metal emissions from MHD facilities has been initiated by the Montana Energy Research and Development Institute (MERDI) but experimental results are not yet available. However, some observations may be made.

The following table summarizes the emissions of mercury from a conventional 775 MW plant (data from Ref. 19)

Mercury In, gm/min			Mercury Out, gm/min	
Coal	Bottom ash	ESP	Flyash	Flue Gas Vapor
1.79	6.8×10^{-2}	4.5×10^{-2}	5×10^{-3}	1.73

Since the boiling temperature of mercury is low, nearly all of the mercury in the coal passes out the stack at the operational temperatures of conventional utilities. Higher temperatures in MHD systems will have little effct on the emission of heavy metals with low boiling temperatures. Thus, based upon a comparison of boiling temperatures (Table 4) MHD plant emissions of (1) mercury, (2) arsenic, and (3) selium should not be significantly different than those of conventional plants. Emissions of zinc, antimony, lead, and cadmium may be marginally larger. If the increase in the emissions of other trace metals is roughly related to its boiler temperature, the emissions of nickel, beryllium, and cobalt for example should be larger. However, the presence of the potassium seed material will also serve to scavenge the heavy metals.

No reported measurements of searches for toxic substances such as carcinogens from conventional plants could be found, and these measurements have not yet been made in the MHD flow-train. Potential carcinogens have been detected in the process of drying and pulverizing Western coal. However, this is not a problem unique to MHD systems. The higher operational temperatures of an MHD system will serve to break such substances down. If they reform in the secondary combustion process or elsewhere in the stream, has not yet been investigated in conventional or MHD plants. However, it appears most likely that the emissions of carcinogenic and chemically toxic substances from MHD systems in all probability not be significantly different than those from conventional plants.

Element	Quantity, ppm	Boiling Temperature, °C
Nickel	7-10	2900
Manganese	0.1-0.3	1900
Zinc	0-5	907
Chromium	0-10	2480
Cobalt	0.5-1.0	2900
Lead	0.5-1.0	1620
Molybdenum	11-16	2620
Vanadium	0-10	3000
Beryllium	0-0.05	2970
Arsenic	0-10	221
Antimony	5-10	1380
Cadmium	0.1-0.3	767
Silver	0-5	1951
Selenium	1.0	688
Mercury	0.4-1.0	356

NO_x and particulate matter. There is a high probability that MHD systems will be able to achieve not only the present-day emission limits for the substances but will also be able to comply with anticipated future emission levels of SO_x and NO_x. The built-in processes for the control of SO_x and NO_x have already been demonstrated, and all test results to date illustrate that present-day and future standards may be met.

Particulate emissions in an MHD system will be small submicron particulate flyash particles coated with potassium sulfate, as well as potassium sulfate particules. Electrostatic precipitators and conventional baghouses may provide the means for collection of solid particulates. The economics and practicality of ESP and baghouse operation for large coal-fired MHD facilities will have to be assessed.

There is no reason to believe that the control of toxic carcinogenic and heavy metal emissions for MHD systems will represent a problem, either in effectiveness, cost, or convenience which is unique to MHD system. However, the emission of these substances from MHD-type facilities should be documented.

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FLUE GAS CLEANING FOR
PRESSURIZED FLUIDIZED-BED COMBUSTORS

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In pressurized fluidized-bed combustion (PFBC), emissions of particles and alkali metal compounds in the flue gas from the combustor may contribute to the erosion and corrosion of hardware. As part of a program to characterize, monitor, and control both particle and alklai metal emissions from PFBC's, information has been obtained on: (1) two light-scattering, particle-size analyzers for on-line measurements of particle emissions, (2) novel techniques for controlling particle emissions, and (3) the removal of the alkali metal compounds from the combustor gases in a high-temperature getter trap.

1. PARTICULATE CHARACTERIZATION AND MONITORING IN PFBC
WITH ON-LINE, LIGHT-SCATTERING PARTICLE ANALYZERS

In the development of pressurized fluidized-bed combustion (PFBC) systems, on-line analyzers for providing continuous particle size and loading analysis would be useful (1) in measuring the efficiency of particulate removing devices (cyclones and filters), (2) in establishing gas turbine performance at different particulate loadings, and (3) in protecting turbines or test cascades in the event of sudden system upsets. In comparison, particulate analysis following batch sampling with probes and inertial impactors in a PFBC system is difficult, and the long time lag between sampling and analysis is a disadvantage.

Two types of optical analyzers using laser light beams, which had not yet been proven for fluidized-bed application, were evaluated. One is a single-particle analyzer developed by Spectron Development Laboratory which characterizes the scattered light from each particle, and the other is a multiparticle analyzer developed by Leeds and Northrup which characterizes the entire particle distribution in its optical path. The results of the evaluation, which have been reported in detail elsewhere,[1,2] are summarized below.

The single-particle analyzer measures the sizes of particles and their velocities by measuring the light scattered from each particle as it crosses an interference pattern generated by the intersection of two laser beams. The region measurement of this instrument, called the probe volume or sample space, is at the center of the duct where the two coherent beams intersect and generate the interference pattern. In this study, three interference fringe periods within the probe volume were used, providing particle size measurement ranges of 4.9-74 μm, 1.5-23 μm, and 0.2-3.1 μm. A more detailed description of the principles of the single-particle analyzer is available in the literature.[3]

scatter incident light. The mean diameter and variance of the particle size distribution can be obtained by examining the total scattering intensity as a function of scattering angle and by comparing the experimental data with theoretical calculations for assumed size distributions.[4] One measured signal is proportional to the volume of particles illuminated and can be used to calculate the concentration (loading) in the gas stream.

If the type of distribution is known (*i.e.*, normal or log-normal), the information on mean diameter and variance completely describes the distribution of the suspended particles. A multimodal distribution cannot be determined, however.

A. Experimental System and Procedure for Flue-Gas Particle Measurements

The flue-gas system of the ANL, 15.2-cm-dia fluidized-bed combustor was modified for these evaluations. Windows for particle analyzers were installed in two locations; one pair was upstream from the primary cyclone. The other windows were near the flue-gas system outlet; there was the capability of routing the flue-gas past these windows from downstream of either the secondary cyclone or a sintered metal filter assembly. With this arrangement, it was possible to size (1) coarse particles entrained from the combustor, (2) smaller particles escaping the two cyclones in series, and (3) particles that had passed through the sintered-metal filters. The particles escaping the sintered metal filters are considered representative of particles that might enter a turbine in a PFBC system.

Downstream from each window location was a sampling port. With the modified flue gas system, particle size measurements were obtained (1) by using the on-line optical particle analyzers, (2) by using an Andersen cascade impactor at the sampling ports, and (3) by analyzing collected steady-state cyclone and/or filter samples with a Coulter counter. In addition, particle loadings could be measured at the sampling ports with glass fiber membrane filters.

Previous FBC studies have shown that measurements of combustion particles with cascade impactors, Coulter counters, and microscopes are in good agreement.[5,6] A comparison was made of particle-size distributions obtained by the cascade impactor and the Coulter counter for particles in the flue-gas between the secondary cyclone and the sintered metal filter. Because the Coulter counter was calibrated with standard particles and its measurements of combustion particles agreed very well with cascade impactor measurements, it was assumed that both of these measurements were representative of the true particle distributions.

B. Characteristics of Suspended Particle Distributions

The total size distribution of particles elutriated from the combustor during a coal combustion experiment (SGL-1) was obtained by combining Coulter counter measurements with sieve analyses of samples collected in the cyclones and metal filter. The fractional mass distribution in successive half-volume

ash ($\rho_a \approx 0.6$ g/cm^3).^{a} Since these materials could not be separated, the distribution could only be obtained by assuming a uniform density; thus, the smaller-diameter fractions, which contain more of the lighter ash and carbon, are probably biased high.

The distribution of the particles escaping through the cyclones during a different coal combustion experiment (SGL-2C) is given in one curve in Fig. 2. The mass loading at this flue gas location is $\sim$0.5-1.1 g/m^3 ($\sim$0.2-0.5 grain/scf), and the mass contribution by particles larger than 10 μm is small. The largest mass fraction consisted of 3.0 to 3.8 μm particles, which contained 22.5 wt % of the total loading. This distribution can be approximately characterized as a log-normal distribution, and it is believed that particles escaping from the sintered metal filter have the same type of distribution. Thus, the type of particle distribution that a gas turbine will see is expected to be approximately log normal.

C. Experimental Evaluation of the Single-Particle Analyzer

Results of particle size measurements obtained with the single-particle analyzer for several combustion experiments performed at 308 kPa pressure have been compared with size distributions determined by Coulter counter measurements and by cascade impactor measurements.

Table 1 summarizes the comparative measurements of particle-size distribution. In experiment SGL-1, the distribution of particles leaving the combustor was measured. For the small-particle size range, the mass log-mean particle diameters obtained were 8.5 μm with the Coulter counter and 20 μm with the single-particle analyzer. For the large particle size range, the mass log-mean diameters obtained were 26 μm with the Coulter counter and 70 μm with the single-particle analyzer. In both cases, the value obtained using the analyzer was $\sim$2.5 times greater than the Coulter counter value.

Table 1. Mass Log-Mean Particle Diameters Obtained with the Single-Particle Analyzer Compared with Coulter Counter and Impactor Measurements

Experiment	Particle Size Range, μm	Single-Particle Analyzer, μm	Coulter Counter, μm	Impactor μm
SGL-1^a	1.5-23	20	8.5	--
SGL-1^a	5-74	70	26	--
SGL-2C^b	1.5-23	18	3.5	--
SGL-1C^b	0.2-3.1	0.72	--	1.6
LASER-4A-2^{b,c}	1.5-23	16	6.0	--

^{a}Sample windows upstream from cyclones.

^{b}Sample windows downstream from cyclones.

^{c}Cold experiment with limestone, no combustion.

In the size range 0.2 to 3.1 μm, the mass log means obtained by analyzer and cascade impactor measurement were 0.7 and 1.6 μm, respectively. Because of the difficulty of measuring submicron particles, the agreement obtained in the 0.2 to 3.1 μm size range is considered to be very good.

For experiments LASER-4A-2, a typical cold experiment, the agreement of the Coulter counter and single-particle analyzer measurements was better than for a typical combustion experiment, as shown in Table 1. However, because the suspended limestone particles were relatively homogeneous, similar in shape, and consistent in light-scattering properties, a better agreement in results would be expected.

It is encouraging that the descrepancy between the two methods of measurement was smaller for the fine particles (< 20 μm). However, a significant difference remained between measurements made with the two instruments for 1.5 to 23 μm particles; diameters measured with the particle analyzer were at least three times the values obtained with the Coulter counter.

Because of the low loadings ($\sim$0.1 g/m^3 or $\sim$0.05 grain/scf) downstream from the metal filter, no size measurements could be made with the single-particle analyzer at this location. Not enough measurable (1.5-23 μm) particles passed through the sample space. However, the present state of the art on turbine technology suggests that the particle size range of 1-10 μm will be significant at loadings of $\sim$0.1 g/m^3 ($\sim$0.05 grain/scf) in causing turbine damage. On-line particle analyzers that can measure particle sizes in this range would be most useful downstream from PFBC particle-removal devices to monitor particle distributions and loadings in the flue gas that enters gas turbines.

D. Experimental Evaluation of the Multiparticle Analyzer

Particle size measurements obtained with the multiparticle analyzer have been compared with particle size measurements made with the cascade impactor. In addition to size measurements, particulate loading measurements were compared.

The measured diameters and loadings for combustion experiments and some cold experiments are given in Table 2. Because the contribution of particles smaller than 1 μm was less than 10%, mass basis, the impactor distributions were not truncated to accomodate the 1-20 μm-dia range of the multiparticle analyzer.

In coal combustion experiments LN-4,-5,-6, and -10 where the gravimetrically obtained loading was relatively high (>0.1 g/m^3), the impactor aerodynamic diameter, $\overline{D}_{AE}$, ranged from 2 to 3.5 μm and the analyzer projected-area mean diameter $\overline{D}_A$, ranged from 2.2 to 3.4 μm. The agreement is considered excellent. For measurements made at lower loading conditons ($\leq$0.01 g/m^3)

measurements at these low loading, D_A was approximately three times D_{AE}.
Since it is difficult to obtain accurate impactor measurements of diameters,
this can be considered fair agreement.

Table 2. Comparison of Particle Sizes and Loadings Obtained with the
Multiparticle Analyzer, the Andersen Impactor, and the Membrane
Filter.

| Exp. | Multiparticle Analyzer | | | Andersen Impactor | | Membrane Filter |
	$\overline{D}_V$ [a] (μm)	$\overline{D}_A$ [b] (μm)	Loading (g/m^3)	$\overline{D}_{AE}$ [c] (μm)	Loading (g/m^3)	Loading (g/m^3)
LN-4-1	5.1	2.8	0.43	2.2	0.33	0.64
LN-4-2	2.9	2.2	0.83	3.5	1.1	1.3
LN-5-1	5.5	3.4	0.18	6.0[d]	0.21	0.41
LN-5-2	3.9	2.3	1.0	3.2	0.98	0.40
LN-6-1	4.4	2.8	0.46	3.0	0.12	0.54
LN-6-2	3.6	2.2	0.64	3.5	1.1	1.0
LN-10-3	3.8	2.2	1.5	2.0	0.56	---
LN-10-4	---	---	0.37	---	---	0.63
LN-11-1	11.9 ± 0.3	5.5 ± 0.1	0.12 ± 0.01	1.9	0.01	---
LN-11-2	---	---	0.13 ± 0.01	---	---	0.009
LN-11-3	10.5 ± 0.2	5.0 ± 0.1	0.11 ± 0.02	1.8	0.01	---
LN-9-3[e]	2.2 ± 0.4	2.0 ± 0.06	0.21 ± 0.04	0.63	0.001	---
LN-9-2[e]	---	---	0.10 ± 0.02	---	---	0.003
LN-9-5[e]	3.8 ± 0.2	2.7 ± 0.07	1.2 ± 0.06	1.5	0.12	---
LN-9-4[e]	---	---	0.5 ± 0.17	---	---	0.110

[a]Volume mean diameter

[b]Projected area mean diameter

[c]Aerodynamic mean diameter

[d]An erroneous value is suspected

[e]Cold experiment; only limestone particles in the flue gas

A comparison of particulate loadings measured by the analyzer, the impactor,
and a membrane filter reveals that for the combustion experiments in which the
loadings were relatively high (>0.1 g/m^3, gravimetric), the gravimetric and
multiparticle analyzer loadings were in reasonably good agreement. At worst,

metric loadings under low loading conditions (<0.01 g/m^3), however, were
generally one order of magnitude less than the optical multiparticle
analyzer loadings. As the approximate maximum tolerable loading for tur-
bines is proposed to be $\sim$0.05 g/m^3 for particles in the range of 1-10 μm,
it is desirable that the optical analyzers be capable of measuring particle
loadings <0.05 g/m^3.

D. Conclusions

The multiple analyzer was a more advanced instrument in its state of
development, allowing it to be used with little operating training. Under
loading conditions of >0.1 g/m^3, the mean particle diameters and particle
loadings obtained using the multiparticle analyzer were generally in accept-
able agreement with measurements obtained using backup techniques. The
single-particle analyzer was, on the other hand, a first generation instru-
ment requiring more sophisticated handling and data reduction. Although
measurements made with the single-particle analyzer did not show as good
agreement with backup measurements as did the multiparticle analyzer, the
potential of the single particle analyzer should be recognized.

2. PARTICULATE REMOVAL FROM FLUE GAS

In pressurized fluidized-bed combustion, the hot flue gas from the
combustor must be expanded through a gas turbine. To prevent erosion of the
turbine blades by particulate matter entrained in the flue gas, the parti-
culate loading must be reduced to acceptably low levels. Although the air
quality requirements for a gas turbine have yet to be experimentally demon-
strated, estimates of what constitute "acceptably low levels" of particulate
mass loading for a gas turbine generally range (depending on the particle
size distribution) from $\sim$0.05 to $\sim$0.005 g/m^3.[7]

Existing devices readily adaptable to high-temperature, high-pressure
particulate removal (e.g., conventional cyclones) are not very efficient
in removing particulate matter with diameters smaller than $\sim$10 μm. Achieving
the "acceptable loading" necessary for PFBC requires, therefore, that highly
efficient methods be developed for removing from flue gas the particulate
solids having diameters between 2 and 10 μm. An experimental program is
under way at ANL to test and evaluate promising flue gas cleaning methods
in the off-gas system of the 15.2-cm-dia fluidized-bed combustor.

A. Granular-Bed Filter

Granular-bed filters currently under development can be generally class-
ified as fixed-bed, moving bed, or fluidized-bed collectors. The collection
concept being considered at ANL is the use of the sulfated limestone from
the FBC as the granular-bed material in a fixed-bed filter with periodic
bed replacement. In the application of this concept, several filter modules

could then be transferred to a regeneration reactor or disposed of.

To test the concept of using the sorbent material in a granular-bed filter, a small test filter (15.4 or 7.8 cm ID) was assembled and installed in the flue gas system of the ANL fluidized-bed combustion process development unit. Due to temperature limitations of the combustor flue gas system, the flue gas is at a temperature of ∿180°C when entering the granular-bed filter. Although these temperatures are far below the operating temperature anticipated for PFBC flue gas cleaning devices (∿900°C), the system does permit testing of the concept, using a flue gas containing particulate dust generated by an operating PFBC.

In a typical test of the granular-bed filter, the fluidized-bed combustion system is brought to steady state and the flow of flue gas is then diverted through the granular-bed test loop. In the test loop, the flow of gas either passes through the granular-bed filter or bypasses it to a sample port where the flue gas is sampled for particulate loading and size distribution, using an Andersen cascade impactor and/or a membrane filter. Experiments were performed with the granular-bed filter to evaluate the effects of filter-bed particle size, bed depth, and gas velocity on the filtration efficiency of the granular-bed.

Experiments to evaluate the effect of bed depth on filtration efficiency were performed at a filtration velocity of 30 cm/s and with beds of virgin dolomite having mean particle diameters of 2120 μm (-6 +14 mesh) or 740 μm (-14 +30 mesh). With the coarser bed material, a least squares linear regression analysis of the experimental data indicates that the filtration efficiency increased from ∿91% at a 5.1-cm bed depth to ∿98% at a 40.6-cm bed depth. In terms of filtration per unit of bed depth, however, the filtration efficiency decreased from ∿18%/(cm of bed) to ∿2.4%/(cm of bed) when the bed depth was increased from 5.1 cm to 40.6 cm.

Similar results for the effect of bed depth on filtration efficiency were obtained with the -14 +30 mesh dolomite bed. Filtration efficiency increased from ∿95% at a 7.6-cm bed depth to ∿97% at a 30-cm bed depth. The small effect of bed depth on filtration efficiency for both the -14 +30 mesh and -6 +14 mesh beds indicates that in both cases filtration occurs at or near the bed surface.

A comparison of the results obtained with the different size bed materials revealed that decreasing the mean bed particle diameter from ∿2120 μm to ∿740 μm reduced the relative penetration (100% - filtration efficiency) of particles through the granular-bed by 35 to 40%.

Tests to assess the effect of gas velocity on filtration efficiency were made with the -6 +14 mesh dolomite at bed depths of 5.1 and 20.4 cm and with a sulfated limestone (mean particle diameter of ∿700 μm) at a bed depth of 5.1 cm. The results were mixed. For the -6 +14 mesh dolomite at a bed depth of 5.1 cm, no change in filtration efficiency (∿92%) was observed at gas velocities of 15, 30, and 60 cm/s. However, for both the -6 +14 mesh dolomite at a bed depth of 20.4 cm and the sulfated limestone at a bed depth

at a gas velocity of 60 cm/s to 99% at 15 cm/s represents an 80% decrease in particle penetration through the bed. The observed effect of velocity indicates that the principal mechanism(s) governing particle removal in the granular bed is other than inertial impaction.

Table 3 presents some selected particle loadings determined by cascade impactors and by membrane filter measurements. Particle loadings in the flue gas leaving the granular bed filter generally ranged from about 0.01 to 0.07 g/m^3. Inlet loadings to the filter were measured to vary from 0.3 to as high as 1.4 g/m^3, with the vast majority of measurements in the range, 0.4 to 0.7 g/m^3.

Table 3. Particle Loadings in the Flue Gas Leaving the Granular-Bed Filter for selected Experiments

Bed Material	Granular-Bed Depth, cm	Gas Velocity, cm/s	Particle Loading in Flue Gas Leaving Granular-Bed Filter, g/m^3	Filtration Efficiency, %
-6 +14 mesh	5.1	30	0.07[a]	91
-6 +14 mesh	5.1	15	0.02[b]	96
-6 +14 mesh	20.3	30	0.07[a]	92
-6 +14 mesh	20.3	15	0.05[a]	95
-14 +30 mesh	5.1	15	0.03[a]	98
-14 +30 mesh	30.5	30	0.006[b]	99
Sulfated	5.1	30	0.02[a]	98
Sulfated	5.1	15	0.02[a]	99

[a] Cascade impactor measurement.

[b] Membrane filter measurement.

When compared with the estimated range of acceptable particle loadings for gas turbine operation, 0.05 to 0.005 g/m^3,[7] the results reported here fall in the higher end of the range.

Mass mean diameters of the dust both entering and leaving the granular-bed were generally of the order of 2 to 4 μm. A comparison of inlet and outlet particle size distributions also revealed that filtration efficiency was constant over the range of dust particle sizes entering the filter, *i.e.*, a 1-μm dust particle entering the granular-bed filter was captured as efficiently as was a 10-μm dust particle entering the filter. This was un-expected and may simply indicate that the sensitivity of the tests was insufficient to measure any effect.

Thus, although the mass loadings in the flue gas leaving the filter were within the range of the estimated requirements, the quantity of >10 µm particles in the effluent gas may prove unacceptable. It should also be emphasized that the cascade impactor provides no information about particle sizes larger than 10 µm. This will have to be determined by other techniques.

The initial pressure drop across the clean bed at the beginning of a filtration cycle for gas velocities below 30 cm/s ranged from a low of ∿1 kPa (4 in. of H_2O) for a 5.1-cm bed of the -6 +14 mesh bed material to a high of 15 kPa (∿60 in. of H_2O) for a 30-cm bed of -14 +30 mesh bed material. Although these pressure drops would be considered excessive in conventional particulate-removal devices, they are not unreasonable for PFBC applications.

A preliminary analysis has also been made to assess the design limitations of the granular-bed filter, assuming that the amount of limestone available for use in the filter would be limited by the quantity of limestone used for the PFBC. For a 200 MW-electric PFBC, the rates of limestone usage and flue gas volumetric flow were used to assess the permissible range of parameters such as bed depth, face velocity, and bed replacement rate for a granular-bed filter. The results indicated that at the filtration conditions of the PDU tests, the limestone requirements of the granular-bed filter would slightly exceed that available from the FBC. The above filtration tests were per-formed, however, under very high particulate loadings to the granular-bed filter and thus very short filtration times and high limestone requirements.

Additional tests are planned following the addition of a high-efficiency cyclone to the flue gas system to evaluate the granular-bed under more realistic conditions of particle loading and size distribution in the flue gas entering the granular-bed filter. This will be necessary before an adequate evaluation can be made of filter performance and of the compatibility of sorbent usage in the PFBC process to material requirements of the granular-bed filter.

B. High-Efficiency Cyclone

A Donaldson Co. TAN-JET cyclone (claimed to have better dust-removal efficiency than conventional cyclones) has been installed in the flue gas system of the ANL 15.2-cm-dia combustor for testing and evaluation. This cyclone will also be useful in further testing of the ANL granular-bed filter concept (discussed above), and in applying acoustic dust conditioning to particulate removal (discussed below).

The TAN-JET employs a secondary flow of clean air to improve gas-solid separation in the primary air flow of dirty gas from the combustor. The secondary air flow is preheated to the temperature of the incoming primary gas flow and enters the cyclone through a nozzle centrally located in the barrel of the cyclone.

A series of experiments has been performed at ambient conditions as a preliminary step to evaluation of the cyclone. For these experiments in

was maintained via a 0.91 m overflow standpipe.

After steady operation was established, the primary and TAN-JET cyclone ash receivers were emptied and a timed period of solids collection was initiated. During this period, the flue gas downstream from the TAN-JET cyclone was sampled at a sampling port using an Andersen cascade impactor. The efficiencies of the primary and TAN-JET cyclone were then calculated from the amount of solids collected in their respective ash hoppers, and the solids loading downstream from the TAN-JET was determined with the cascade impactor.

The results of the experiments are summarized in Table 4. Three experiments were performed at each of three levels of pressure drop ($\sim$70, $\sim$100, and $\sim$140 kPa) across the TAN-JET secondary air inlet nozzle. At 70, 100, and 140 kPa pressure drop across the nozzle, the secondary air flow represented $\sim$10, $\sim$12, and $\sim$13% of the total gas flow (primary plus secondary) through the TAN-JET cyclone, respectively.

Table 4. Results of Preliminary Experiments in Evaluation of TAN-JET Cyclones

| ΔP Across TAN-JET Nozzle (kPa) | Expt. No. | Combustor (g/m³) | Particle Loading Leaving | | Particle Collection Efficiency | | |
			Primary Cyclone (g/m³)	TAN-JET Cyclone (g/m³)[a]	Primary Cyclone (%)	TAN-JET Cyclone (%)	Combined (%)
$\sim$70	2	12	0.62	0.11	95	81	99.0
	6	17	1.1	0.17	94	82	98.9
	8	31	1.5	0.14	95	90	99.5
$\sim$100	1	5.0	0.29	0.08	94	69	98.1
	5	25	1.4	0.12	95	90	99.5
	9	13	0.69	0.13	95	79	99.0
$\sim$140	3	2.3	0.34	0.08	86	74	96.4
	7	18	1.5	0.12	92	90	99.2
	10	12	1.2	0.14	90	86	98.6

[a]Total air (main air flow plus secondary air)

The solids loading in the flue gas leaving the cyclone ranged from a low of 0.08 g/m³ to a high of 0.17 g/m³. Collection efficiency ranged from 69 to 90%.

The TAN-JET collection efficiency data has been correlated as percent penetration (100% - collection efficiency) as a function of the mass loading

nozzle ΔP on the collection efficiency. Penetration at a given inlet mass loading would be expected to decrease with increasing nozzle pressure drop.

The mass loading in the flue gas leaving the TAN-JET has also been correlated as a function of the mass loading in the gas entering the TAN-JET cyclone. Although the correlation exhibits considerable scatter, it does indicate that the increases in cyclone efficiency with increasing inlet mass loading are insufficient to prevent the outlet mass loading from increasing also. This is an expected result.

The lowest measured mass loading of 0.08 g/m³ leaving the TAN-JET cyclone is equivalent to the highest measured mass loadings in the granular-bed filter tests described above. Tests are currently being performed to evaluate TAN-JET performance during combustion. Considerably more effort will be required to establish TAN-JET cyclone efficiency by particle size.

C. Acoustic Dust Conditioning

Acoustic dust conditioning (ADC) is a technique to enhance the natural tendency of polydispersed particles to impact upon each other and agglomerate. Thus, the use of acoustics in controlling fine particle emissions is a process whereby the mean size of the effluent particles is significantly increased by exposure to high-intensity finite-amplitude acoustic fields. As described, acoustic dust conditioning is designed to increase the collection efficiency of downstream dust collectors.

Efforts to date have been carried out under a subcontract to the University of Toronto* for development and fabrication of a pulse-jet acoustic dust conditioning (PJ-ADC) system. Components of the system include (1) a pulse-jet (PJ) sound generator, (2) a resonant manifold system (RMS) to match the acoustic system capacity with the FBC system capacity, and (3) an acoustic treatment section (ATS) where the flue gas can be exposed to the acoustic field.

Although the merits of PJ-ADC as applied to PFBC have been reviewed,[8] the basic reasoning supporting the development effort are repeated here:

1. PJ-ADC has achieved 5- to 7-fold increases in the mean particle diameter of industrial type aerosols.[9]

2. Performance evaluations indicate that high-efficiency cyclones may reduce solids loadings sufficiently to meet gas turbine inlet criterion for particle loading if the mean particle diameter entering the cyclone is increased by a factor of 2 to 5.

3. Pulse-jets are combustors, and exhausting the heat of combustion from pulse-jets directly into the off-gases from the PFBC would add to the internal energy of the flue gas; therefore, this heat

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The effort at the University of Toronto was divided into three phases: Phase 1, the design, fabrication, and testing of a pulse jet-resonant manifold system (PJ-RMS) at atmospheric pressure, has been completed. Phase II, increasing the operating pressure of the PJ-RMS to ~1.01 MPa, has been initiated. Phase III, which is to be the design, manufacture, and testing of a PJ-RMS system for installation and evaluation in the flue gas system of the ANL fluidized-bed combustion process development unit, is yet to be initiated.

The results of the work at the University of Toronto have been very encouraging. Major uncertainties surrounding the development of the PJ-RMS have been removed, and the effort to date has yielded no evidence that the technical objectives of the project cannot be met. However, the project has involved significantly greater developmental work than was originally anticipated. The following summarizes the results obtained to date: Emphasized are the advances made in pulse jet technology during the developmental effort.

Phase I completion was signified by the steady state, continuous operation of a high-frequency, high-sound-intensity pulse-jet exhausting into a tuned resonant manifold operating at approximately ambient conditions. Sound intensities as high as 160 dB have been achieved while frequencies of ~300 Hz were maintained. Although the absence of definitive and quantitative diagnostics prevents unequivocal claims regarding pulse-jet performance, it appears reasonable to claim that (1) the achievement of ~160 dB sound levels at 300 Hz exceeds the sound levels previously achieved at these frequencies by pulse-jets and (2) the use of a resonant manifold can be used to increase the total sound production, as well as to increase the frequency of the resonant combustion.

Phase II progress is signified by successful operation of the PJ-RMS at pressures as high as 350 kPa. No operational difficulties were caused by those increased pressures. There is reason, in fact, to believe that the sound levels increased with increased operating pressure. Operation of the pulse-jet at pressure constitutes another significant advance in pulse-jet technology.

Although the developmental work necessary to extend the operating characteristics of pulse-jet designs has been significantly greater than anticipated, the feasibility of PJ-ADC for PFBC continues to look promising. Continued examination of PJ-ADC in high temperature/high pressure applications is planned.

3. FIXATION OF FLUE-GAS ALKALI-METAL COMPOUNDS

In the prospective application of pressurized fluidized-bed combustion (PFBC) of coal to power generation, corrosion and erosion of the turbine

A way to accomplish this is use of a hot granular-bed filter with a suitable bed material to simultaneously remove alkali metal compounds and particulates.

Research work has been under way at Argonne National Laboratory to develop effective granular sorbents that can be used as bed material in a granular-bed filter for the removal of alkali metal compounds from the hot flue gas of PFBC. Presented in this part of the paper are (1) experimental results obtained in screening six commercial products using gaseous alkali metal compounds transported in hot simulated flue gas of PFBC and (2) preliminary cost evaluations of the two most effective sorbents.

A. Experimental

A laboratory-scale, batch-type, fixed-bed combustor system was used for this study. The system has been described elsewhere.[10] The reaction vessel is a 8.9-cm-ID 1.8-m-long horizontal stainless steel pipe and consists of preheating, combustion, filtration, and cold-trap sections. The sorbent is placed between two perforated steel plates in a stainless steel tube, which is fastened on the upstream side of a cold trap tube into which a cold finger is inserted; the sorbent functions as the filter in the filtration section of the combustor. A weighed pure alkali metal compound is heated in the combustion section of the combustor (which section is heated by induction heating) and is vaporized. The vapor is carried by preheated flowing gas downstream through the sorbent bed and finally is condensed on the cold trap tube, cold finger, and the backup filter (a glass-wool filter).

Six commercial products, Alundum (Pure α-Al_2O_3), Celatom MP-91 diatomaceous earth (Eagle-Picher Industries, Inc., Ohio), Silica Gel, Burgess No. 10 pigment (Burgess Pigment Company, Georgia), Attapulgus Clay, and activated bauxite (the last two from Engelhard Minerals and Chemicals Corp., N.J.) have been screened as sorbents for the removal of gaseous NaCl and KCl from simulated hot flue gas of PFBC. Before each test, each sorbent was pretreated in a flowing air stream at 900°C to remove volatile alkali metal compounds. All tests carried out in this study were performed with -8 +10 mesh sorbent at atmospheric pressure. The volumetric composition of the simulated flue gas used was 3% O_2, 16% CO_2, 180 ppm H_2O, ~300 ppm SO_2, ~80 ppm alkali metal compound vapor, and the balance N_2.

At the end of each experiment, the weight loss of alkali metal compound in the sample pan was measured; the condensates from the cold trap were collected by washing with distilled water and were analyzed for the alkali metal of interest. Sodium in the water solution was analyzed by flame emission spectrometry, and potassium was analyzed by atomic adsorption spectrometry. For the analysis of chloride ion, a potentiometric method was used. The sorbent was analyzed for alkali metal by wet chemical methods to measure its effectiveness in removing gaseous alkali metal compounds from flue gas.

alkali chloride vapor-bearing air flow or alkali chloride vapor-bearing simulated flue gas of PFBC. The sorbents were tested at an average bed temperature of 875°C. As shown in this table, diatomaceous earth and activated bauxite are the two most effective sorbents for capturing both NaCl and KCl vapors. The NaCl vapor sorption efficiencies of diatomaceous earth, activated bauxite, and Burgess No. 10 pigment are noted to increase greatly in the tests in which simulated flue gas was the NaCl vapor-carrying gas. This increase is the result of the combined effects of (1) shorter experiment duration, (2) higher NaCl vapor concentration in the flue gas, and (3) the higher superficial gas velocity of flue gas, which increases the mass transfer of NaCl vapor from the bulk of the flue gas to the surface of the sorbent, thereby increasing the sorption of NaCl vapor by the sorbent.

With the promising results obtained from these screening tests, systematic studies have been made to investigate the effects of several operating variables on the NaCl vapor sorption performance of diatomaceous earth and activated bauxite. Results of these studies show that:

1. The capture capacities for these two sorbents are related to their internal surface areas, increase with temperature for diatomaceous earth but decrease with temperature for activated bauxite, and increase with a decrease of the gas hourly space velocity of flue gas.

2. The rates of capture by both sorbents are independent of the superficial gas velocity of flue gas in the range of 25 to 155 cm/s, indicating that the capture rate is not mass transfer controlled. .

3. NaCl vapor was primarily tied up by diatomaceous earth in chemical forms that are not soluble in water; in contrast the NaCl captured by activated bauxite can be largely leached out by a simple water-leaching process, indicating the regenerability of activated bauxite for reuse.

The details of these studies will be presented elsewhere.[11]

C. Preliminary Cost Evaluations of Diatomaceous Earth and Activated Bauxite Used for the Removal of Alkali Metal Compounds from Hot Flue Gas of PFBC

The effectiveness of both diatomaceous earth and activated bauxite (alkali-sorbents) for the removal of alkali metal compounds from hot simulated flue gas of PFBC has been experimentally demonstrated. The cost evaluation presented here is intended to gain preliminary information on the cost of material of diatomaceous earth and activated bauxite used as alkali sorbents, as compared with the SO_2-sorbent required in PFBC combustors for sulfur removal. Table 6 shows assumptions and computation bases

Table 5. Material Balances for NaCl and KCl from Testing Sorbents for NaCl and KCl Vapors Capture. Sorbent bed temperature

Experiment No., HGC-	3	4	5	6	7	8	11	11R	12R	13	16	17
Sorbent	Alundum	Diatomaceous Earth	Silica Gel	Burgess No. 10 Pigment	Attapulgus Clay	Activated Bauxite	Diatomaceous Earth	Diatomaceous Earth	Activated Bauxite	Burgess No. 10 Pigment	Diatomaceous Earth	Activated Bauxite
Flowing Gas	Air →					→	Simulated Flue Gas →					→
Superficial Gas Velocity, cm/s	8 →					→	25 →					→
GHSV[a], h^{-1}	3,500 →					→	12,000 →					→
Experiment Duration, min	180 →					→	100 →					→
Input												
(1) NaCl or KCl Transported[b]	92	91	91	92	95	96	242	303	245	252	321	271
Output												
(2) NaCl or KCl Collected by (a) Cold Traps	71	18	40	15	25	6	6	8	3	26	3	10
(b) Glass-wool Filter	24	6	15	5	9	2	4	4	5	13	1	4
(3) Total	95	24	55	20	34	8	10	12	8	39	4	14
(4) % NaCl or KCl Capture by Sorbent 100x[(1)−(3)]/(1)	−3	74	40	78	64	92	96	96	98	85	98	95

Total NaCl, mg

Total KCl,

[a] Gas hourly space velocity of flowing gas passing through the sorbent bed.

[b] Amount of NaCl vapor or KCl vapor transported to the sorbent bed and cold trap.

Assumptions for 200-MWe PFBC Demonstration Plant

(1) Coal: Typical Illinois Coal with a heating value of 12,500 Btu/lb and an ultimate analysis of 70.3% C, 5.0% H, 1.3% N, 3.3% S, 11.4% Ash, and 8.7% O.

(2) SO_2-Sorbent: Tymochtee Dolomite containing 51.8% $CaCO_3$ (20.7% Ca) and 43.3% $MgCO_3$; once-through operation.

(3) Excess Air: 20%

(4) Ca/S Mole Ratio for 80% S Removal: 1.5

(5) Over-all Cycle Efficiency: 40%

Computation Bases for Alkali-Sorbent Evaluation

(1) 90% removal of alkali metal compounds from hot flue gas (at 800°C) assumed to contain 28 ppm (by vol.) alkalis at a linear velocity of 66 cm/s (2.2 ft/s) and GHSV = 33,500 h^{-1}. (This basis is derived from the experimental results obtained from both diatomaceous earth and activated bauxite at 800°C and atmospheric pressure operations)

(2) Bulk Density of Granular Sorbents (ρ: given by manufacturer)

$$\rho_{D.E.} = 24 \text{ lb/ft}^3 \text{ (385 g/L)}$$

$$\rho_{A.B.} = 55 \text{ lb/ft}^3 \text{ (882 g/L)}$$

(3) Current Price of Granular Sorbents (August 1978)

$80/ton of diatomaceous earth

$275/ton of activated bauxite

$8/ton of SO_2-Sorbent (assumed)

(4) Once-through operation for alkali-sorbents

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for this preliminary cost evaluation for a 200-MWe PFBC demonstration plant, and estimated costs are given in Table 7.

As compared with the 0.82 mil cost per KWe-h electricity produced for SO_2 sorbent, 0.22 and 1.64 mils are estimated to be the costs for using diatomaceous earth and activated bauxite, respectively, to achieve 90% removal of alkalis from the hot flue gas of PFBC produced from a 200-MWe demonstration plant. Although the cost for activated bauxite is about eight times that of diatomaceous earth, activated bauxite can be regenerated. The cost of regeneration and the number of cycle that activated bauxite can be regenerated without losing its sorption activity are not known now. More study is needed to allow more detailed evaluation of this sorbent.

Sorbent	Sorbent Required per ton of Coal Burned, lb	Cost of Sorbent per ton, $	Cost of Sorbent per KWe-h Produced mil/KWe-h
SO_2-Sorbent	601	8	0.82
Diatomaceous Earth	16	80	0.22
Activated Bauxite	35	275	1.64

To the present, neither a reliable measurement of the level of total alkali in PFBC flue gas nor the level of alkalis in PFBC flue gas tolerable by a gas turbine is available. Based on thermodynamic calculations, researchers at General Electric Company have estimated that the alkali vapor present in the flue gas of PFBC will approach 10 ppm when 0.1% Cl coal is combusted at 950°C; on the basis of gas turbine liquid fuel experience, that level of alkali vapor may be up to two orders of magnitude greater than the acceptable limit for a gas turbine.[12] According to this information, 90% removal of alkalis from flue gas may not be sufficient to meet the acceptable limit for a gas turbine. However, both diatomaceous earth and activated bauxite can theoretically achieve higher removal efficiency at high pressure (10 atm) and longer contact time or shorter GHSV ($\sim 33,500 \ h^{-1}$). Further tests of these two sorbents to investigate the effects of pressure and alkali concentration in flue gas on the sorption performances are warranted and are pursued in this program.

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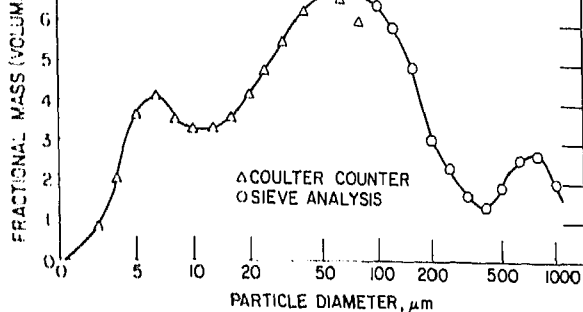
Fig. 1. Fractional Mass Distribution of All
Elutriated Particles during a Com-
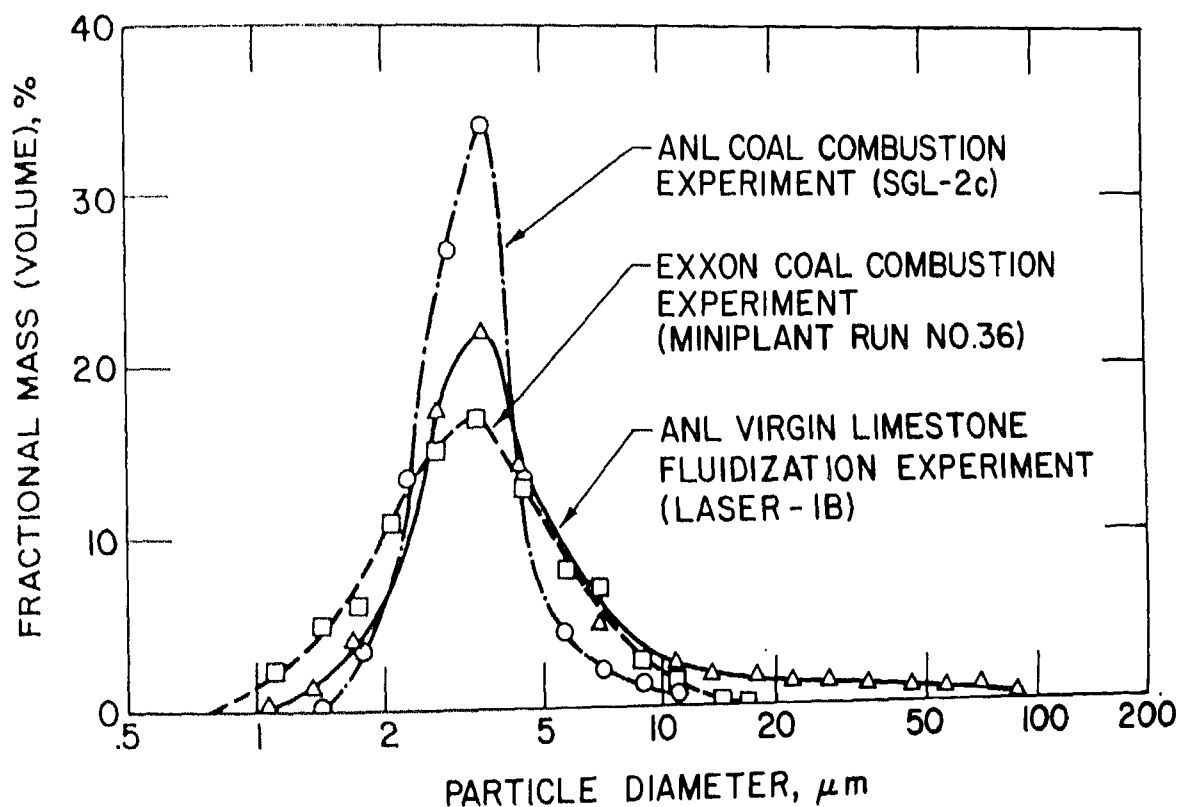bustion Experiment (SGL-1) from the
ANL PFBC

Fig. 2. Fractional Mass Distribution of Particles
Escaping PFBC Flue Gas System Cyclones.
Determined by Coulter Counter Analysis

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1. INTRODUCTION

Fluidized-bed combustion (FBC) systems are being developed to burn coal in an environmentally acceptable manner for the production of electrical power or industrial steam. In these systems, coal is combusted in a fluidized-bed of calcium oxide-containing solids, usually limestone. In the presence of excess oxygen, the calcium oxide in the system reacts with the SO_2 released in coal combustion to form calcium sulfate ($CaSO_4$). A FBC system thus acts as an *in situ* SO_2 emission control system. The partially sulfated stone mixed with some coal ash and the fly ash constitute the main solid waste streams from the fluidized-bed combustor. The fly ash is similar to that obtained from conventional pulverized coal furnaces but contains some partially sulfated limestone. The waste sorbent stream consists of partly sulfated and calcined limestone, *i.e.*, a mixture of $CaSO_4$, CaO, $CaCO_3$ with an admixture of coal ash.

In those applications in which dolomite is used, the sorbent waste consists of $CaSO_4$, CaO, $CaCO_3$, MgO (the MgO does not sulfate under the conditions found in the fluidized-bed combustor), and coal ash. The amount of $CaCO_3$ found in the sorbent waste depends on the pressure in the FBC system. In atmospheric-pressure systems, the amount of $CaCO_3$ is small; in some pressurized FBC systems, significant amounts of $CaCO_3$ are found in the sorbent waste.

The amount of sorbent waste generated by a FBC system depends on the sulfur content of the coal and the ratio of limestone to coal (*i.e.*, the Ca/S mole ratio) which must be fed to the bed to achieve the flue gas SO_2 level which is required to meet EPA emission standards. The limestone to coal ratio depends on the reactivity and SO_2 capacity of the limestone and the operational parameters of the FBC system. The main operational variables are the system pressure, bed temperature, and air flow rate.[1]

Pope, Evans and Robbins reported[2] that in a typical atmospheric-pressure FBC system, a Ca/S mole ratio of 3.2 was needed to achiev EPA SO_2 emission levels when burning a coal containing 4.1% sulfur. This ounted to feeding 0.6 kg of limestone for each kg of coal burned. St e ANL[3] showed that a Ca/S mole ratio of 1 was required in a pressuriz B tem when using a coal containing 3% sulfur and dolomite as the sorbe his coal-sorbent combination, 0.25 kg of dolomite must be used for k coal burned. Comparison of these results shows that a large amou e waste can be expected when high-sulfur coal is burned.

To reduce the quantities of sorbent waste, re availa (1) the SO_2 capacity of the limestone can be inc se of ch al reaction enhancement agents such as sodium chlor mestone be regenerated and reused in the combustor (*i.e.*, r a syn ic sorbent can be made which can be used for mor cy busto an can

2. LIMESTONE REACTIVITY ENHANCEMENT BY CHEMICAL TREATMENT

The use of chemical additives to increase the SO_2 capacity of limestones when used to control the SO_2 emission from FBC's was suggested by Pope, Evans and Robbins.[4] They found that the addition of sodium chloride increased the extent of sulfation of the limestone. Their experience over a period of several years was that there was a considerable improvement in the removal of sulfur dioxide from the flue gas of their AFBC when sodium chloride was added. The use of salts to regulate the properties of limes has been used by the lime industry for a long time. The use of salts to improve the SO_2 capture efficiency of limestone when used in a fluidized-bed burning oil shale was patented by Berglund *et al.*[5]

Proceeding on the basis that mineralizing salts affect the porosity of a stone during reaction and that the porosity is important to SO_2 reactivity, experiments were designed to test this assumption and to characterize the effects of various mineralizers. Sulfations were carried out using Greer limestone to measure quantitatively the effects of various salts on the reaction. How reactivity varied with concentration of salt (introduced by soaking the stones in hot solutions) was examined for $NaCl$, Na_2CO_3, Na_2SO_4, KCl, and $CaCl_2$. The magnitude of the effect differed for different salts, but all of these salts were effective in promoting sulfation. Sodium chloride increased the calcium utilization from 25% to 60% (or more than a factor of two) for Greer limestone. Further tests were performed using sodium chloride with a series of limestones of various compositions and morphologies. The objective of these tests was the characterization of various limestones with respect to their reactivity enhancement by mineralizing salts. The results of these studies have been published.[6] It has been concluded that in reactions with sulfur dioxide, the porosity of the reacting stone is of major concern. Specifically, a narrow range of pore size is required to produce a stone having maximum reactivity towards sulfation. Smaller pores do not remain open, during sulfation, and larger pores have very low surface area. For limestones, the optimum porosity lies near 0.3 μm "average" pore diameter as calculated in this work, and for dolomites optimum porosity is near 0.14 μm "average" pore diameter.

The major effect of salt addition is to cause trace amounts of surficial liquids to be present, thereby increasing the ionic mobility of the system. The increased diffusion of species allows rearrangement and recrystallization to occur, changing the pore structure of the stone and allowing more sulfation to occur than would occur without salt addition. By suitable choice of the amount of salt, the pore structure can be optimized for sulfation. The interaction is a function of the composition and morphology of the original stone, and optimum amounts and types of salt additions can be chosen on the basis of induced changes in porosity. The quantity of salt needed appears to be very small--on the order of 1.0 mol % (∿0.5 wt %) for both limestones and dolomites. Larger amounts of salt may actually reduce the reactivity of the stone with respect to sulfation.

waste limestone substantially. By suitable adjustment of working conditions and the quantity of mineralizers, economically unreactive stones could be brought up to a level of SO_2 absorption capacity that would enable them to compete with naturally reactive stones. The use of these marginally reactive stones could reduce the dependence on a particular limestone. Local quarries might then be able to provide suitable bed material for fluidized-bed combustors. In areas where intermediately reactive stones are abundant, the use of salts to enhance reactivity could substantially reduce the total amount of stone necessary for a given SO_2 reduction.

3. REGENERATION OF SULFATED STONE FOR REUSE IN FBC

Regeneration of the CaO in the spent sorbent and recycling it offers an additional method of reducing the potential waste disposal problem caused by the spent sorbent. Sulfated sorbent can be regenerated by reductively decomposing $CaSO_4$ to CaO at temperatures of $\sim 1100°C$ in a fluidized-bed reactor in which the heat and the reductants required are produced by incomplete combustion of coal in the fluidized bed. A typical solid-gas reaction by which regeneration occurs is: $CaSO_4 + CO \rightarrow CaO + CO_2 + SO_2$. The buildup of CaS, which is formed by competing reactions in the reducing environment, is minimized by the presence of an oxidizing zone at the bottom of the fluid bed where fluidizing air is introduced.

The feasibility of a sorbent regeneration process will depend on (1) the ability to regenerate the stones and to generate an SO_2-rich off-gas which can be treated in a sulfur recovery process without imposing a heavy economic burden on the power plant, (2) the reactivity of the regenerated sorbent during subsequent utilization cycles, and (3) the sorbent's resistance to decrepitation remaining at acceptable levels.

A series of experiments has been performed in the ANL process development unit fluidized-bed regeneration system to obtain rate data for regeneration of Tymochtee dolomite. The effects of the sorbent's residence time (7-35 min) in the reactor, the regeneration temperature (1000-1100°C), and the pressure (115-153 kPa) on the extent of CaO regeneration and the SO_2 concentration in the off-gas have been obtained. The experimental regeneration rate data for both of these experiments have been statistically analyzed and presented elsewhere.[7,8] The extent of regeneration increases with increasing bed temperature and with increasing solids residence time.

The feasibility of sorbent regeneration depends partially on the ability to recycle the sorbent a sufficient number of times (1) without loss of sorbent reactivity for either sulfation or regeneration and (2) without severe attrition. If either of these requirements is not met, the sorbent makeup rate will be too high to justify regeneration. The changes in reactivity, the changes in regenerability, the extent of decrepitation, and the extent of ash buildup were evaluated in a ten-cycle (sulfation-regeneration) experiment using Tymochtee dolomite with no sorbent makeup. These experiments have been detailed.[9] A second set of experiments have been done using Greer limestone.[10]

dry off-gas from the regenerator ranged from 6-9%. In the combustion part
of the cycle, it was found that by using a constant CaO/S mole feed ratio of
1.5, the sulfur retention decreased linearly--from ∿88% in the first combustion
cycle to ∿55% in the tenth combustion cycle.

Based on calcium balances around the experimental systems at steady-state
conditions, attrition losses during combustion were ∿16% during the first cycle
and ∿5% during the remaining nine cycles. The sorbent losses during regener-
ation averaged ∿2% per cycle. Thus, the average combined loss due to attrition
and/or elutriation per cycle was ∿8%.

Sorbent losses due to attrition and elutriation essentially establish the
lower limit of the fresh sorbent makeup rate. The actual makeup rate is depen-
dent on the combined sorbent utilization losses due to both attrition and
changes in reactivity. High makeup rates would be required for stones that
easily decrepitate or readily lose reactivity; therefore, it would not be
feasible to regenerate such stones.

An analysis was made of the cyclic utilization sulfation data to estimate
the sorbent makeup requirements (the ratio of makeup sorbent to the total or
makeup plus recycle sorbent) for a continuous combustion-regeneration process.
The analysis shows that low makeup rates can be achieved by using high recycle
rates. On the basis of this estimate a makeup CaO/S ratio as low as ∿0.2 (at
a total CaO/S mole ratio of ∿1.4) should be sufficient to meet the EPA sulfur
emission limits (estimated for a coal containing 2.8% S for which a 70% retention
is needed).

4.   SYNTHETIC SO$_2$ SORBENTS

It may be possible to decrease the environmental impact of the sorbent
waste from fluidized-bed combustion by using synthetic SO$_2$ sorbents instead of
naturally occurring limestones.

A variety of metal oxides in a support material (*e.g.*, α-Al$_2$O$_3$) were con-
sidered as synthetic sorbents. The alkali and alkaline earth metal oxides
Na$_2$O, K$_2$O, CaO, SrO, and BaO, have the highest reactivity with SO$_2$ in the high-
temperature range of 805-950°C where fluidized-bed combustors typically operate.

The synthetic sorbent, CaO in α-Al$_2$O$_3$, presently is the most promising
synthetic sorbent for use in fluidized-bed coal combustors to minimize SO$_2$
emissions. K$_2$O and Na$_2$O in alumina have higher sulfation rates; however, their
products (sulfates) decompose in the temperature range of interest for combustion
and regeneration. These compounds contribute to corrosion of metals at high
temperatures. Calcium oxide is the least expensive of the metal oxides tested.
CaO sorbents capture more SO$_2$ per unit weight of sorbent than do barium oxide or
strontium oxide; therefore, calcium oxide is the metal oxide of choice. The
choice of α-Al$_2$O$_3$ as the support material was based on its stability in the
temperature region being considered. The calcium aluminates also add to the
mechanical strength of the sorbent, minimizing attrition.

therefore, large pores in the support (with diameter larger than about 0.2 μm) are beneficial. Sorbents containing higher CaO concentrations are less porous. However, the optimum CaO concentration depends on the residence time required in the combustor and the CaO concentration effect on sorbent strength, since the quantity of SO_2 captured per unit weight of sorbents in a given time is independent of the sorbent's CaO concentration.

Natural sorbents (dolomite or limestone) contain higher concentrations of CaO than do the synthetic sorbents and therefore capture more SO_2 per unit weight of material. Thus, more synthetic sorbent material may be needed for each pass through the combustor (possibly twice as much). However, with regeneration of synthetic sorbent, the overall consumption of synthetic sorbent should be lower. A detailed report of these studies has been published.[11]

5. COMPARISON OF OPTIONS FOR REDUCING THE QUANTITY OF SOLID SORBENT WASTE

The three options may be compared by estimating the quantity of fresh sorbent needed and the waste sorbent produced per unit of electrical power. The environmental impact will be proportional to the sum of these quantities. The quantity of sorbent needed depends on (1) the sulfur content of the coal (and its heating value), (2) the reactivity of the sorbent, as measured by the Ca/S mole ratio that must be used to meet the EPA standards, and (3) the CaO content of the sorbent. If sorbent is recycled, less fresh sorbent will be needed, the quantity depending on the number of cycles achievable.

A simple numerical example illustrates these factors. Consider an atmospheric-pressure fluidized-bed combustor using coal which contains 4% sulfur and has a heating value of about 2.8×10^7 J/kg. To meet the EPA standard of 0.26 g of sulfur emitted per 10^6 J (0.6 lb per 10^6 Btu), about 82% of the sulfur must be removed from the flue gas before it is vented to the atmosphere. The Ca/S mole ratio depends on the reactivity of a sorbent under the operational conditions of the FBC. Variables such as bed temperature, gas velocity, limestone particle size, and residence time of the limestone, (and if the combustor is a pressurized unit, the pressure), need to be specified.

Work reported by Pope, Evans and Robbins[2] with Greer limestone, indicates that a Ca/S ratio of about 3.1 would be needed to obtain 82% sulfur retention in their AFBC operating at about 816-832°C (1500-1530°F) with a 3.8-4.7 m/s (12.5-15.5 ft/sec) superficial gas velocity. About 0.36 kg/h of coal is required for 1 kWh of electricity. Therefore, 0.36 x 0.04 = 0.014 kg or 0.45 mole of sulfur is produced per hour per kWh(e). Hence 0.45 x 3.1 = 1.4 moles of calcium must be fed per hour. Since Greer limestone is 80% $CaCO_3$, 180 g/h per kWh (e) must be fed to the AFBC to achieve the needed sulfur emission control. About 26% of the $CaCO_3$ content of the limestone is converted to $CaSO_4$ [computed from the ratio of retention percent (82%) and Ca/S mole ratio (3.1)]. The remaining $CaCO_3$ would be calcined, leaving the bed as CaO. When these chemical changes are taken into account, the quantity of the waste is found to be 140 g/h per kWh(e).

temperature of 870 C and a gas flow rate of 0.89 m/s. Since this dolomite con-
tains only 53% $CaCO_3$, it is found that about 190 g/h per kWh(e) is needed.
About 37% of the $CaCO_3$ is converted to $CaSO_4$. The remaining $CaCO_3$ and all of
the $MgCO_3$ (40%) are calcined. The quantity of partially sulfated dolomite waste
is computed to be 130 g/h per kWh(e).

The effect of NaCl on the reactivity of Greer limestone was reported by
Pope, Evans and Robbins.[2] When NaCl was added, the 82% sulfur retention could
be achieved using a Ca/S ratio of 2.2. Under these conditions, 120 g of lime-
stone would be needed per hour per kWh(e) and 75 g of waste would be produced
per hour per kWh(e).

If regeneration is used, it is expected that only 0.2 as much fresh dolomite
would be needed; hence the above values for dolomite would become 40 g/h per
kWh(e) feed and 25 g/h per kWh(3) waste.

Estimation of the expected performance of synthetic sorbents is made uncer-
tain by the fact that they have not been tested in a FBC. It is therefore nec-
essary to estimate the Ca/S ratio needed by comparing their reactivities as
measured in the laboratory (TGA experiments) with the reactivities of natural
stones which have been tested in a TGA and the FBC. When this is done, a synthet-
ic sorbent containing 20% CaO is estimated to require a Ca/S ratio of about 5
in a AFBC to achieve 82% sulfur retention. Based on this ratio and the conser-
vative estimate that a 4% fresh feed is needed, about 25 g/h per kWh(e) of syn-
thetic sorbent is needed. The waste quantity is about 27 g/h per kWh(e). All
of these estimates of environmental impact are summarized in Table 1.

Table 1. Comparison of Environmental Impacts of SO_2-Emission Control Methods
for Fluidized-Bed Combustion (4% Sulfur Coal)

Combustor Type and Control Option	Sorbent g/h per kWh(e)	
	Fresh Feed	Waste
AFBC, Limestone One use and discard	180	140
AFBC, Dolomite, One use and discard	190	130
AFBC, Limestone NaCl treatment, one use and discard	120	75
AFBC, Dolomite Regenerate 20% makeup rate	40	25
AFBC, Synthetic sorbent Regenerate 4% makeup rate	25	27

Three options for the reduction of the quality of solid sorbent waste from a fluidized-bed combustor have been studied. The estimated quantity of waste generated using regeneration and synthetic sorbents was about the same and significantly lower than a once-through use or the use of chemical additives. The use of chemical additives is expected to reduce the solid waste by a factor of two when compared to a once-through use of the stone. The choice between these options will ultimately need to be based on the cost. The relative costs are not developed in this paper, however, our studies indicate that synthetic sorbents (of the type developed in this study) would be two to three times the cost of a once-through use of natural stones. Studies reported elsewhere[12] indicate that the break even cost (*i.e.*, cost the same as a once-through use of natural stones) of the limestone needs to be between about $10 to $12 per ton for the reductive decomposition process reported in this paper.

7. ACKNOWLEDGEMENTS

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